



# THERMODYNAMICS

## FOR CHEMICAL ENGINEERS

BY

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NEW YORK

JOHN WILEY & SONS, INC.,

LONDON: CHAPMAN & HALL, LIMITED

1939

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Printed in U. S. A.

Printing  
F. H. GILSON CO.  
BOSTON

Composition  
AL COMPOSE  
BOSTON

Binding  
STANHOPE BINDERY  
BOSTON

## PREFACE

Thermodynamic methods of analysis are extensively used by two quite different groups. The chemist, representative of the first, is primarily interested in problems where chemical reaction occurs. Very often the quantity of matter under observation is enclosed in an apparatus to prevent interchange of material between the system and the surroundings. Moreover, the chemist often carries out his experiments under conditions at least approaching those of constant temperature and pressure. His interest may be purely scientific. He will be inclined to place major emphasis on changes of a reversible, isothermal, non-flow nature. Under these circumstances analysis in terms of free energy is direct and satisfactory.

The engineer, and more particularly the mechanical engineer, must deal with changes where conditions approximate those of steady flow. Usually the changes are physical rather than chemical. For high efficiency, heat loss and frictional effects of all kinds must be eliminated as far as is economically possible. To this end, mechanical equipment, such as engines and turbines, is designed to approximate adiabatic reversible operation. The mechanical engineer finds the use of the entropy concept convenient under these conditions.

The chemical engineer, however, must be familiar with both methods of interpretation. He must be able to correlate the two different approaches, utilizing whichever is more convenient in the solution of the particular problem under consideration.

In this book an attempt has been made to present the more important thermodynamic relations in a manner particularly useful to the chemical engineer.

When using this book for undergraduate instruction it will probably be found that the first fourteen or fifteen chapters include as much material as can be covered satisfactorily in a two-semester course. Familiarity with the fundamentals of physics will be useful, and the simultaneous study of physical chemistry, as practiced in many schools, will be helpful. To some this may appear to involve unnecessary repetition, but considerable experience with undergraduate instruction in thermodynamics has indicated that few students are able to master this subject without some repetition.



As new material is covered it will be helpful to reinterpret problems of earlier chapters in the light of more advanced understanding. Thus the exercises at the end of Chapter II may be solved in terms of general mathematical expressions just after this chapter is covered. Later when the properties of vapors, such as steam, and the perfect gases have been studied they may be repeated and solved for numerical answers by assuming that the fluid under discussion is first steam and then a perfect gas. Still later these same problems may be used for calculation of change in such functions as entropy, free energy, or availability. This method serves to impress on the student the importance of first analyzing a problem in terms of fundamental thermodynamic principles and, in addition, the fact that this analysis is not dependent on the particular material undergoing change.

The aid an author receives from his associates during the preparation of a manuscript does much to lighten the task. Dr. Warren K. Lewis was most helpful. His numerous suggestions and friendly criticism are gratefully acknowledged. Among the many others who have aided are Mr. Thomas B. Drew, Dr. Robert L. Hershey, Mr. Fred L. Chase, Jr., and especially Dr. Robert York, Jr. I wish to express my appreciation to Mr. Thomas B. Drew and Dr. James A. Beattie for reading the manuscript critically and to Professor Joseph H. Keenan for suggestions in connection with Chapters XII, XIII and XIV.

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CAMBRIDGE, MASS.  
*July, 1939*

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# THERMODYNAMICS FOR CHEMICAL ENGINEERS

## CHAPTER I

### FUNDAMENTAL CONCEPTS OF THERMODYNAMICS

**Introduction.** Clear precise thinking is imperative if one is to avoid the pitfalls of thermodynamics. To this end a thorough understanding of the various terms is a necessary prerequisite. Unfortunately many of these are loosely used while others are so fundamental in character as almost to defy exact definition. In the pages immediately following, the more important concepts have been either defined or outlined. With a clear understanding of such fundamentals as energy, temperature, heat, and work, it is possible to derive, with the aid of a few experimental facts, the whole extensive and somewhat complicated superstructure of thermodynamics. Without a clear understanding of the fundamentals, proficiency in analyzing the more complex problems can never be attained.

Though the student may feel that he understands these fundamentals through long acquaintance, he is urged to read these earlier pages carefully and to make sure that he has mastered each idea before proceeding to the next. Only by this procedure can later difficulties be avoided.

**Energy.** In almost every branch of knowledge assumptions must be made at the outset. Thus in geometry the axioms are facts supposedly so self-evident that their truth is unquestioned. Similarly in thermodynamics it is necessary to agree on certain facts. But these are so broadly recognized that their truth is universally accepted. Admitting the reality of matter, one is quickly forced to assume the existence of a "something" associated with matter which profoundly influences its properties.

A bullet in motion has properties differing from those of the same bullet at rest. An iron ball exposed to the sun has properties differing from those of the same ball when cold. Similarly a body magnetized or charged electrically has characteristics not possessed by the same body without the magnetic or electrical influence. Even a book resting on a shelf is capable of causing effects which the same book cannot cause

if it is placed on the floor; *e.g.*, if allowed to fall to the floor, by a suitable mechanism, it can be made to raise a weight.

To explain these phenomena we postulate the existence of energy, an entity to explain the workings of the universe.

Energy can be detected only by its action on matter. It may appear in many forms. If easily segregated into a single form, it is usually given a special name. The moving bullet possesses energy of motion, kinetic energy; the ball in the sun has been struck by radiant energy. The magnetized body possesses magnetic energy, and the electrical charge is said to consist of electrical energy. The book on the shelf because of its position possesses potential energy over and above that possessed by the same book on the floor.

The energy released when a chemical reaction occurs is often loosely called chemical energy, and experiment teaches that all bodies have associated with them energy due to vibration, rotation, and relative position of the molecules, often roughly called internal energy.

The oft-repeated statement that energy is capacity for doing work is unsatisfactory and surely can be of but little use until a definition of work has been formulated.

**Definitions of Common Terms.** As the science of thermodynamics developed, new terms were introduced. In themselves these represented no fundamental principles. They are so convenient for thermodynamic analysis that the student should acquaint himself with them.

TABLE I  
COMMON THERMODYNAMIC PROCESSES

Type of Change	Condition of Restraint Imposed on System
Adiabatic.....	No heat interchange with surroundings
Isothermal.....	No temperature change
Isometric.....	No volume change
Isobaric or isopiestic.....	No pressure change

The thermodynamic **system** is the body of matter under discussion. Wisdom in the choice of a suitable system in the more complicated cases is important in thermodynamic analysis. The quantity of matter in a given system is usually restricted to the minimum compatible with the problem in hand. Thus, in the problem of gas compression the gas may be taken as the system excluding the compressor proper.

An **isolated system** is one which can exchange neither energy nor matter with the surroundings.

## TEMPERATURE

A **process** is any kind of change or transformation, physical or chemical, a thermodynamic system may undergo. Several important types of changes are listed in Table I.

A system is in a definite **state** when its properties are fixed.

A system is said to have undergone a **change in state** if any or all of its properties are changed, and a change in state is definitely determined when the initial and final conditions are given.

If a series of transformations results in returning a system to its original state, the complete change is called a **cycle** or **cyclical process**. This does not imply that conditions in the surroundings are unchanged.

**Temperature.** To clarify what is meant by temperature let us consider two solid bodies, *A* and *B* (see Figure 1), isolated from their surroundings. Grant, for the moment, that they exert no appreciable electrical, magnetic, chemical, or similar effects

on each other. Bring the bodies into contact except for an intervening rigid wall, which allows passage of energy but prevents passage of matter. Experimentally, one of two results is always found: both bodies undergo a physical change (Figure 1*a*), or no change (Figure 1*b*) is observed in either. Never does one change but not the other, although if the masses differ greatly the fractional change in the larger may be small. A third body, *C*, is now taken. If it is found that *A* in contact with *B*, as above described (Figure 1*c*) does not change, and *B* in contact with *C* likewise does not (Figure 1*c*), then *A* brought into contact with *C* never changes

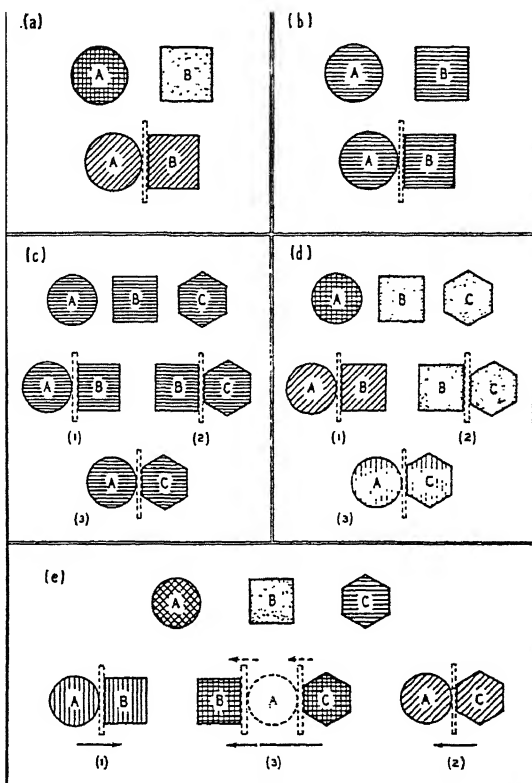


FIG. 1. The Concept of Temperature.

(Figure 1*c*). Furthermore, if  $A$  in contact with  $B$  (Figure 1*d*) undergoes a change, but  $B$  in contact with  $C$  does not, then  $A$  in contact with  $C$  always changes. Moreover, the initial change in the properties of  $A$  is in the same direction as when  $A$  was in contact with  $B$ . Finally (Figure 1*e*), if  $A$  in contact with  $B$  changes in a given direction, while  $A$  in contact with  $C$  changes in the opposite, then bringing  $B$  into contact with  $C$  results in changes in both, the initial directions of which are identical with those resulting from contact of both bodies with  $A$ .

Moreover, in experiments where a change was noted some of the bodies would have felt hotter than others. By touching, probably not much difficulty would have been experienced in arranging the objects in order, starting with the coldest and finishing with the hottest. In experiments where no change was evident all bodies involved would have felt equally hot.

From the preceding discussion it is evident that, even with the restrictions imposed for these experiments, there still exists an actuating force. This property is called **temperature**, a characteristic property of these bodies. It is the first of several **potentials** to be encountered in this text. The relative magnitude of a potential determines the direction of physical interaction.<sup>1</sup> Change in any property of matter can result only if there is a difference in potential or "driving force."

**Measurement of Temperature.** Probably the idea of temperature was based originally on the physiological sensations of hot and cold. These highly qualitative methods were soon replaced by quantitative investigations. Differences in temperature may be detected and their values determined by employing as a measure or meter a substance, the change in some property of which is readily subject to quantitative measurement. Any of the bodies  $A$ ,  $B$ , or  $C$  might serve as such a meter. Devices embodying this principle are called thermometers.

In the oldest and most common type of instrument a liquid is contained in a glass vessel. Change in volume of this liquid is the physical property employed to determine the temperature. Liquid-in-glass thermometers were constructed and our present thermometric scales established more than two centuries ago.

<sup>1</sup> To avoid effects of surface tension and the like, each body should be brought up to the intervening wall in the absence of the other and its properties noted. If the properties remain unchanged when both bodies are at the wall, their potentials are equal in their positions adjacent to the wall, but may have changed approaching it. Surface effects are, however, usually negligible. While magnetic, electrical, mechanical, and gravitational effects may occasionally complicate the thermal interactions of bodies, proper allowance can be made for these. Such complications do not limit the validity and generality of the statements here given.

**Liquid-in-Glass Thermometers.** Early investigators in thermometry standardized on the use of liquid-in-glass instruments, particularly mercury in glass. For thermometers containing different liquids, each instrument was calibrated by indicating upon it its so-called fixed points, *i.e.*, its readings at the freezing point and boiling point of water under atmospheric pressure, the intervening space being subdivided into a specified number of divisions of equal length, 100 on the Centigrade scale and 180 on the Fahrenheit scale, the scale being extended similarly beyond the fixed points. It was found that instruments thus constructed containing various liquids checked closely (except for special liquids such as water, which exhibit a maximum density with temperature). If, however, in an instrument thus calibrated, the liquid was replaced by another, even though the quantity of this was adjusted to make the instrument read correctly at any one specified temperature, its readings were no longer even approximately correct at other temperatures.

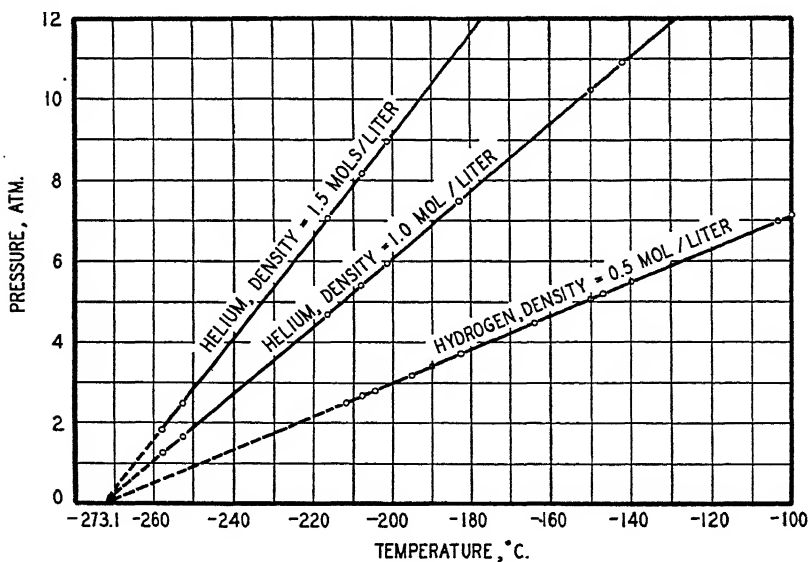


FIG. 2. Constant Density Extrapolation of Gas Pressure to Zero.

**Gas Thermometers.** When investigators began to study the behavior of gases, they discovered two interesting facts. First, the pressure of a gas held at constant volume (or the volume of a gas held at constant pressure) is a linear function of the temperature measured by the liquid thermometer. Extrapolation of the curve of pressure versus temperature (or volume versus temperature) for gases to zero pressure (or vol-



## FUNDAMENTAL CONCEPTS OF THERMODYNAMICS

ume) shows that the temperature at which the pressure becomes zero is 273.1 degrees below the Centigrade zero. Such an extrapolation is shown in Figure 2, which is based on data from the "International Critical Tables." Second, and even more surprising, was the discovery that, if in a given instrument, the gas were replaced by another, using a quantity such that the pressure (or volume) reading was identical at one chosen temperature, all other readings would remain practically unchanged with the new gas.

Minor deviations were encountered, but they were small and tended to vanish the lower the pressure at which the experiments were conducted. The pressure-volume characteristics of a gas were found to be a function only of the temperature and independent of the nature of the gas. This experimental fact — that at low pressures the coefficient of expansion is the same for all gases — is in sharp contrast to that for liquids.

TABLE II  
CUBICAL COEFFICIENTS OF EXPANSION AT ONE ATMOSPHERE\*

Gases (0–100°C.)	Coefficient
NH <sub>3</sub> .....	0.00380
CO.....	0.00367
CO <sub>2</sub> .....	0.00372
H <sub>2</sub> .....	0.00366
NO.....	0.00372
<hr/>	
Liquids (20°C.)	
Hg.....	0.00018
C <sub>6</sub> H <sub>6</sub> .....	0.0012
CS <sub>2</sub> .....	0.0012
H <sub>2</sub> O.....	0.0021
Ethyl ether.....	0.0017
CCl <sub>4</sub> .....	0.0012
C <sub>5</sub> H <sub>12</sub> .....	0.0016
Acetone.....	0.0015

\*International Critical Tables," Vol. 3, pp. 6–16; "Smithsonian Physical Tables," pp. 283–284, 1933.

**Heat.** The idea of temperature as a potential implies the existence of an entity which can be transferred from one body to another. This transfer can be detected by a change in physical properties. The entity is called **heat**. Heat is a form of energy moving under the influence of temperature difference.

## EXPANSION WORK

Assume that the force exerted on the fluid through the piston is but differentially less, at any instant, than that exerted by the fluid. After the piston has moved a distance  $dL$ , corresponding to an expansion (of the fluid)  $dV = A dL$ , the fluid will have done an amount of work on the piston

$$dW = (\text{Force}) (dL) = P dV \quad (1)$$

Knowing a relation between  $P$  and  $V$ , one may immediately integrate and evaluate the work done between any two prescribed limits. Often this relation is involved, and the integration is best performed graphically by means of a plot on the  $P$ - $V$  plane. On such a plot the area under the curve, *i.e.*, between the curve and the  $V$  axis, gives  $\int P dV$ , the work done by the fluid (Figure 3).

Although Equation 1 is a most important means for evaluating expansion work, an appreciation of its limitations must be kept in mind. These may be analyzed by reference to the specific case under consideration.

1. The fluid can do no expansion work if there is no acceptor to absorb the energy. Thus a fluid expanding into an evacuated space of fixed size can do no expansion work on the surroundings.

2. A fluid cannot perform its *full* expansion work if the retaining walls are moving too rapidly. Under such conditions, a pressure gradient will be set up in the expanding material and the total expansive force cannot be exerted on the walls. Fortunately, most fluids expand rapidly enough so that, in the systems usually encountered, this factor is negligible.

3. A fluid can perform its full expansion work on the surroundings only when the fluid pressure is at all times but differentially greater than the surroundings pressure.

Only for changes where these limitations hold is it possible to calculate the work actually done on the *surroundings* from an integration using the  $P$ - $V$  values for the *system*. In all other cases the work must be determined from the surroundings, irrespective of the pressure-volume

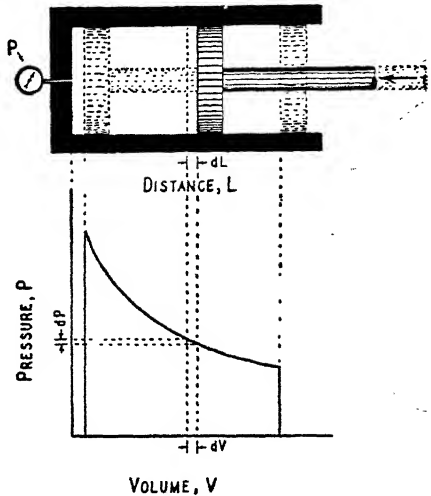


FIG. 3. Evaluation of Reversible Work of Expansion.

relations for the system. This is an important and often overlooked point.

The acceptor, the body absorbing the expansion work, may vary widely in nature. It may be the moving piston in a cylinder, or the liquid displaced by a gas entering an apparatus. A body entering a space already occupied by a fluid must force the fluid out of the way; this requires the expenditure of work by the entering body on the fluid being displaced. A common example is the pushing back of the atmosphere inherent in the evolution against atmospheric pressure of any gas or vapor, whether the evolved gas mingles with the air being forced back or is separated from it by an intervening membrane, such as the walls of a container, *e.g.*, a gas holder. This displacement work against atmospheric pressure must be done when any body, solid or fluid, is evolved or ejected into a space made available by displacement of the air. Work of expansion can also be imparted as mechanical energy to the "surroundings" of the body chosen as the system by pressing upon another body of the same material moving ahead of the one in question. A common example of this sort is that in which the material ahead has kinetic energy imparted to it because of an increase in its velocity, as is true when steam passes through a turbine nozzle. Another form of acceptor for expansion work is condensing vapor, when maintenance of pressure is required for continuance of condensation.

**Electrical Work.** This is a result of moving a quantity of electricity against an electrical pressure or potential difference. Mathematically

$$W_e = CE = EI\theta \quad (2)$$

where  $W_e$  = electrical work done by the system, joules.

$C$  = quantity of electricity flowing, coulombs.

$E$  = electrical potential, joules/coulombs, or volts.

$I$  = rate of flow of electricity, coulombs/second, or amperes.

$\theta$  = time, seconds.

Often electrical work added to a system is used to bring about electrochemical changes as in the manufacture of chlorine and sodium from sodium chloride. The full work of the electrical energy added can be completely used in causing the desired chemical change only if conditions paralleling those required for complete utilization of expansion work be fulfilled. More especially this necessitates that the potential set up by the system be but differentially less than that of the electricity being supplied from the surroundings. Methods of ensuring this require consideration of factors which can best be studied at a much later chapter.

In changes where electrical work effects are important, due allowance must also be made for any expansion work effects, such as evolution or absorption of gas as a result of chemical changes brought about by the electrical work. The total work effect must include both of these.

**Direction of Temperature Scale.** Quantitative conversion of work to heat enables one to determine the logical direction for any temperature scale.

For example, choose as an experimental substance some material such as a block of metallic copper and attach to it a thermometer. By rubbing this block on a rough surface such as a heavy rug, add work. This will be quantitatively and completely converted to heat. It seems logical to say that addition of heat to a body increases its temperature, and the temperature change as a result of this expenditure should be called positive.

To make certain that addition of heat to a body will change its temperature the body must be held at constant volume. This limitation is closely approximated in the experiment here suggested. Had work been added to water at  $100^{\circ}\text{C.}$  and at a constant pressure of 1 atm., no change in temperature would have been detected, but the volume would have been increased.

**Reversible Processes.** A thermodynamic process is **reversible** if, at any stage, a differential decrease in potentials causing the change will result in reversal of the process itself, both in direction and in all its quantitative effects. In most cases reversal will not progress beyond a differential amount unless the conditions are progressively modified as the change continues. It is obvious that no change can be reversible if at any stage temperature or other potential differences are greater than infinitesimal. After a reversible change, it is possible to restore both the system and surroundings to their original conditions.

To visualize one important type of reversible process, assume a horizontal cylinder containing a fluid (Figure 4) and fitted with a tight, frictionless piston. Assume the character of the fluid and the conditions under which it exists such that the product of its volume and the pressure it exerts is constant. At a given instant the fluid has a volume  $V$ . The pressure  $P$  will develop on the piston a total force,  $F$ , the product of the pressure and the area of the piston. If there is exerted upon the piston a second external force exactly equal and opposite in direction, the piston will have no tendency to move in either direction. If, however, this externally imposed force is reduced differentially, the piston will be acted on by a net unbalanced force tending to move it outward. This outward motion will increase the volume of the fluid and decrease its pressure.

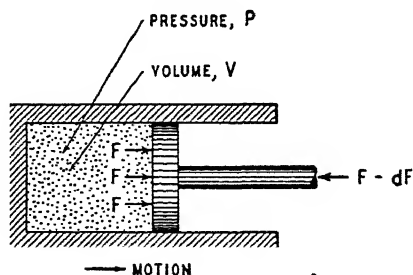


FIG. 4. Example of a Reversible Process.

However, this externally imposed force is reduced differentially, the piston will be acted on by a net unbalanced force tending to move it outward. This outward motion will increase the volume of the fluid and decrease its pressure.

Only a differential increase in volume is necessary to reduce the expansive force on the piston below that of the externally imposed force. Consequently, motion will cease unless the latter force is again reduced. Progressive modification of the counterbalancing force can cause either continued expansion or compression of the fluid. At each point the expansive and externally imposed forces differ only infinitesimally in magnitude. It might, therefore, seem difficult to adjust accurately the opposing force at each instant, but this is not the case. If, as is usual, adjustment of the pressure throughout the mass of fluid is rapid, and the piston or the mechanical system with which it is connected is heavy, the force exerted by the expanding fluid on the piston accelerates the piston thereby generating a countervailing force exactly equal and opposite to that exerted by the fluid. As a result the work done by the expanding fluid is *quantitatively* converted into kinetic energy of motion of the piston and its associated parts. "Acceptance" of the fluid's expansion energy by the piston is even more automatic if the piston is connected with some energy-absorbing mechanism, such as a flywheel or an electric generator.

No process involving a volume change can be reversible unless an effective mechanism exists by which the surroundings can quantitatively absorb (or furnish) the work corresponding to the change.

In general a process is reversible only when all driving potentials involved are at every instant but differentially greater than those opposing. A transfer of heat could be accomplished reversibly if the body accepting the heat were always but differentially cooler than the body losing the heat. *No process involving friction can be reversible.*

To transfer a finite amount of energy or to do a finite amount of work by a reversible process would take an infinite time. The reversible process is a limiting case which may be closely approximated but never actually realized.

**Irreversible Processes.** Referring again to the horizontal cylinder containing the frictionless piston, assume the external opposing force always far less than the force of the expanding fluid. If the piston is of light weight, the fluid will not be able to expand fast enough to maintain its full pressure against the piston face. The piston will try to move away from the fluid. This will result in a pressure gradient in the fluid, the lowest pressure at the piston face and the highest at the cylinder head. Although the piston may be stopped and its kinetic energy usefully employed, perhaps in generating electricity, the gradient established because of the rapid piston motion will be destroyed by swirling and mixing in the cylinder. The gradient might conceivably have been utilized by sliding across the cylinder a large number of diaphragms dividing the fluid longitudinally into differential sections, each at a different pressure from its neighbors. By connecting suitable engines between the various sections the gradient could have been neutralized

with the production of work in addition to electricity previously produced. The combined electrical and hypothetical engine work would, if used with maximum efficiency, just be sufficient to restore the cylinder, its contents, and the surroundings to their original condition. Actually no effective mechanism to utilize fluid pressure gradients existed, and in place of the possible engine work, an increase in the energy stored in the fluid will appear as the result of the swirling action. Without this engine work, the electrical work will be insufficient to restore the cylinder, its contents, and surroundings to their original condition. This is an irreversible process. The cylinder and its contents may be restored by "borrowing" from the surroundings an amount of work equal to the lost engine work. But then the surroundings cannot be restored to their original conditions. Hence, an irreversible process always causes changes which can never be completely undone.

#### SUMMARY

The existence of energy having been assumed as an aid in describing the workings of our universe, it was possible to explain temperature in terms of experimental results. **Heat** was defined as that particular form of energy in transit moving under the influence of a temperature difference, while **work** includes all those forms of energy in transit which are quantitatively and completely interconvertible.

For clarity and record the following definitions are given:

The **system** is the quantity of matter under discussion.

A **process** is any change suffered by the system.

A **cycle** is any process or series of processes in which the system is returned to its original state.

A **reversible process** is one such that, at any stage, a differential decrease in the driving force will cause the process to proceed in the opposite direction. After a reversible change, both the system and surroundings may be restored to their original conditions. After an irreversible process, the system and surroundings can never be completely restored.

## CHAPTER II

### THE FIRST LAW OF THERMODYNAMICS THE LAW OF THE CONSERVATION OF ENERGY

In the previous chapter certain fundamental concepts were discussed and in addition several terms were defined. This chapter deals with generalized equations expressing the results of countless *experiments* all of which point to the conclusion that energy can neither be created nor destroyed. After any change the system and surroundings contain the same amount (although not necessarily the same kinds) of energy as before.

Because of this it is possible to write an energy balance for any process. This balance may be expressed by one of two closely related but somewhat different equations.

The first or **non-flow equation** is applied to processes where the quantity of matter as a whole is not in motion.

The second is useful for processes where the material under discussion is flowing through an apparatus, as air passing through a pipe or steam through a turbine. For lack of a more suitable name the equation for flow processes is called the **flow equation**. Practically always it is applied to changes where there is no depletion or addition of matter during the process.

Both are expressions of the first law of thermodynamics — the law of energy conservation.

**The Law of Energy Conservation.** Let us consider any system originally in state *A*, transformed by any conceivable path or series of paths to state *B* and then returned again along any chosen path to *A*, the only limitations being that a change occurs and that thereafter the system be returned to its o

*By experiment* it is always found that, in general,<sup>1</sup> when a system passes from *A* to *B* there is a *net* interchange of energy between it and the surroundings. When the system is returned to its original condition *A*, there is a second interchange of energy, this time exactly equal and opposite to that experienced in passing from *A* to *B*.

<sup>1</sup> This is always true except when states *A* and *B* are so chosen that in each the energy of the system is the same.

Since energy can be detected only by its influence on matter, the statement that the system has been returned to its first state is equivalent to saying that it possesses the same energy as originally. Moreover, as the experiments indicate, the surroundings now possess the same amount of energy as originally. Repeated experimentation has never disclosed any unexplained discrepancy from these facts. For clarity and conciseness, the experimental results are usually referred to as the law of energy conservation, the **first law of thermodynamics**. The amount of energy in any system and its surroundings is fixed and unchangeable.

**Internal Energy.** The energy of a mass of matter under given chemical and physical conditions (in a definite state) is called its *internal* or *intrinsic* energy. It will be designated by the symbol  $E$ . No assumptions as to the cause or inherent character of this energy will be made, although in certain specific cases its nature will be investigated. The energy of a compressed spring is internal, although that part due to the compressed form of the spring is not usually investigated by the broader technique of thermodynamics but rather by the methods of mechanics.

When ice melts, that energy flowing to the ice as heat will be found stored in the resulting water as part of its internal energy. Similarly, the heat passing to the surroundings on mixing sulfuric acid and water has come from the internal energy originally stored in the water and acid, and, after the process is completed, this heat will be found stored as part of the internal energy of the surroundings. In these examples changes in volume due to the process are neglected. Fuels contain large amounts of internal energy released in part by allowing them to burn with the oxygen of the air.

For convenience we sometimes separate certain parts from the *total* internal energy associated with a body, and give these specific names. Thus the moving bullet previously mentioned has **kinetic energy** of motion as well as **potential energy** due to its elevation. The other energies associated with this bullet are grouped together and called merely its internal energy. Similarly, electrical or magnetic effects may sometimes be included as part of an internal energy, but more often they are treated as though they were separate forms of energy.

Broadly speaking, all energy not in transit might be classed as internal, although specifically one often separates from the whole those quantities of energy which lend themselves to special analysis, and gives to them special names such as kinetic, potential, magnetic, and electrical, reserving for the residue the term internal energy. Although the beginner may feel that this makes for ambiguity, such



is not the case and but little difficulty will be experienced in this connection.

Since energy is detectable only by its influence on matter, it is readily seen that a system in a given state will *always* have the same internal energy. Thus after a cyclical process the system must have the same internal energy as before the process took place. A system may also have the same internal energy at different states. Several examples illustrating this will be presented later.

**Internal Energy Changes.** In the light of our present knowledge, it is impossible to determine the total internal energy of a body. Consequently, discussion must be limited to differences in internal energy between specific states or conditions. Such a difference in internal energies is represented by  $\Delta E$ . Often it is convenient to choose some arbitrary datum, corresponding to a definite condition of the material, as a level above or below which energy can be measured (e.g., 1 atm., 32°F.).

**Internal Energy a Point Function.** The internal energy of a system is completely determined by stating the conditions of the system irrespective of the path by which the state was attained. Such a function, independent of the path, is called a **point function**. The internal energy of any system is a point function. It is the first of many such used in thermodynamic work. Mathematically the differential of a point function is a complete, exact, or perfect differential and has all the properties mathematicians ascribe to such.

Summarizing, any given body of matter can be considered as an energy reservoir, which may be filled or emptied within specific limits, the energy content being determined absolutely by the physical and chemical conditions under which the matter exists. To determine the kind and amount of the energy only the present state of the material need be known; no knowledge of past history is required.

### THE FIRST LAW EQUATION

Let us examine in some detail the energy changes between a system and its surroundings. Initially the system has a total energy (all internal)  $E_1$ . Any energy interchanged between the system and surroundings must be transferred as heat or work. Since no interchange of matter is assumed, there is no other possible form for the energy in transit. But after a process involving an energy interchange with the surroundings, the total energy (all internal) of the system is  $E_2$ . The difference between the heat withdrawn from the surroundings  $Q$  (an energy gain to the system) and the work

(an energy loss by the system) must equal the change in internal energy,  $E_2 - E_1$ . Stated mathematically<sup>1</sup>

$$Q - W = E_2 - E_1 = \Delta E \quad (1)$$

For a differential change

$$dQ - dW = dE \quad (2)$$

Either expression is called the first law equation.

The equation in these forms applies only to systems in which there is interchange of energy (heat and work) but not of matter with the surroundings. This is frequently expressed by saying that it applies to non-flow (batch) processes in which a segregated amount of matter is submitted to a definite series of transformations. Almost all quantitative chemical analyses come under this head. In chemical industry ordinary operations of digestion and many such chemical reactions as batch neutralization, oxidation, reduction, and incineration are examples of non-flow processes.

Ordinarily the system's internal energy above some datum plane will be known at the start and end of the process and  $\Delta E$  may be evaluated by simple difference between the two irrespective of the path. On the other hand, both  $Q$  and  $W$  depend on the path followed. Usually it is more convenient to calculate  $W$ , getting  $Q$  by difference between this and  $\Delta E$ .

The work  $W$  may appear in one or more different forms, but, of these, expansion and electrical work are of outstanding importance.

**Application of First Law to Conditions of Steady Flow.** The steady flow of fluids through a system, or apparatus, is a problem of unusual importance in engineering work. Although, in chemical work, one frequently encounters cases involving a number of streams, discussion will first be limited to those of a single stream. The assumption will be made that there is no net increase or depletion in the amount of matter contained in the apparatus. The flow is called "steady" if the amount of matter entering the system per unit time equals that leaving, and in addition the values of all variables such as pressure, temperature, and density remain unchanged at any point in the apparatus although they need not necessarily be the same at all points.

Visualize a fluid stream flowing through a conduit into some sort of apparatus, and out a second conduit. (Figure 1.) Let  $S_1$  refer to a

<sup>1</sup> In this book  $Q$  will be positive when heat is withdrawn from the surroundings;  $W$  will be positive when work is done on the surroundings. Care must be exercised to keep these signs consistent as failure to do so will lead to error and misunderstanding.

specific section taken at right angles to the path of fluid flow in the entering conduit, and  $S_2$  to a second specific section similarly chosen in the conduit through which the fluid leaves. Between sections  $S_1$  and  $S_2$ , the fluid is restrained by walls through which no matter can pass, but through which energy (heat or work) may flow.

To determine the various energy effects consider a differential amount of fluid,  $dm$ , entering the apparatus at the section  $S_1$ . It is perhaps

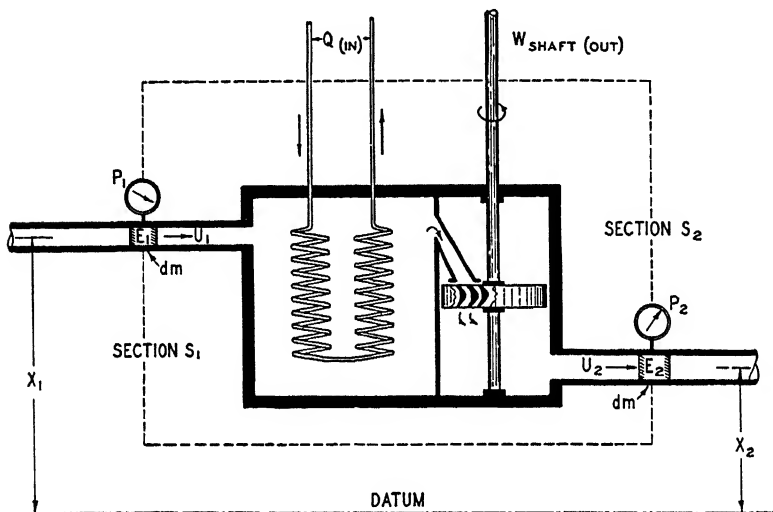


FIG. 1. Energy Relations for Steady Flow.

best to visualize it as segregated from the rest of the fluid by two thin, weightless membranes, each a sort of imaginary piston. Call the internal energy *per unit mass*<sup>1</sup> of fluid as it passes section 1,  $E_1$ . Then the internal energy brought into the apparatus by the fluid at this point is  $E_1 dm$ . Let the section  $S_1$  be a distance  $X_1$  above an arbitrarily

<sup>1</sup> In the English system several units of mass are in common use. Fundamentally the pound is a unit of force or weight, and correspondingly the mass or quantity of matter would be the weight divided by the gravitational constant at the point where the weight was determined. If the unit of mass is taken as one pound, the corresponding unit of force is the poundal, about one thirty-second of the usual force of one pound. Engineers often use the pound as a unit of force and simultaneously as a unit of mass. For measurements performed at one point where the gravitational constant  $g$  is fixed no difficulty arises, but if measurements are made at various points the value of  $g$  corresponding to the point where each individual measurement is made must be used in evaluating the different energy terms. Since  $g$  changes but slightly even over great distances, usually a single value is used for evaluating all the energy terms in the overall energy balance.

assumed horizontal datum plane. The fluid entering will possess an amount of *potential energy*,  $X_1 dm$ , recoverable by allowing it to fall from  $X_1$  to the datum. The pressure at the section  $S_1$  is  $P_1$ , and the specific volume at that point,  $V_1$ . The body of fluid,  $dm$ , has a volume,  $V_1 dm$ . It is pushed into the apparatus in question through the section  $S_1$  by the fluid flowing behind it, and this fluid therefore does *work* upon the differential amount of fluid equal to its pressure times its volume, *i.e.*,  $P_1 V_1 dm$ . If the fluid is moving through section  $S_1$  with a velocity  $U_1$  it brings into the apparatus a quantity of *kinetic energy*,  $(U_1^2/2g) dm$ . Similarly, at section  $S_2$ , the fluid leaving the equipment carries out the corresponding energy quantities  $E_2 dm$ ,  $X_2 dm$ ,  $P_2 V_2 dm$ , and  $(U_2^2/2g) dm$ . This is true because steadiness of flow requires that in any given time interval the quantity of fluid passing any two sections must be the same. During its passage through the equipment, however, the fluid may have received energy as *heat*,  $Q dm$ , and as *shaft work*,  $-W_{\text{shaft}} dm$ , where  $Q$  and  $-W_{\text{shaft}}$  are the quantities of heat and work picked up in the process *per unit quantity* of fluid flowing. Allowance has now been made for all energy quantities affecting the fluid.<sup>1</sup> An energy balance may be written

$$dm + X_1 dm + P_1 V_1 dm + \left( \frac{U_1^2}{2g} \right) dm + Q dm - W_{\text{shaft}} dm = E_2 dm + X_2 dm + P_2 V_2 dm + \left( \frac{U_2^2}{2g} \right) dm \quad (3)$$

This simplifies to

$$E_1 + X_1 + P_1 V_1 + \left( \frac{U_1^2}{2g} \right) + Q - W_{\text{shaft}} = E_2 + X_2 + P_2 V_2 + \left( \frac{U_2^2}{2g} \right) \quad (4)$$

or letting  $\Delta$  denote (Final value) - (Initial value),

$$Q - W_{\text{shaft}} = \Delta E + \Delta(PV) + \Delta\left(\frac{U^2}{2g}\right) + \Delta X \quad (5)$$

This equation is the steady-flow form of the first law equation for a single stream. Each term in the equation is representative of an energy effect. For purposes of calculation, all terms must be expressed in the same units (see Appendix I for conversion factors). Moreover, the equation as derived refers to *unit mass* of material flowing.

It is assumed that all electrical, magnetic, and similar effects are either absent or are included in the term  $W dm$ . Otherwise the necessary terms to allow for such effects must be added to both sides of the general equation.

In deriving the flow equation it was assumed that  $X$ ,  $P$ ,  $V$ ,  $U$ , and  $E$  have definite, constant values over the whole of each cross section. Because of hydrostatic head and other effects, this is usually not true. Ordinarily, these variations introduce negligible errors. In some problems, however, failure to allow for variation in the velocity over the cross section may cause appreciable or serious error.

It is important to note the close similarity between this first law expression and that for the non-flow process. For convenience, Equation 5 may be rearranged

$$Q - W_{\text{shaft}} - \Delta(PV) = \Delta E + \Delta X + \Delta \frac{U^2}{2g} \quad (6)$$

The work done by (or on) the fluid as a result of its expansion (or contraction) is

$$W = W_{\text{shaft}} + \Delta(PV) \quad (7)$$

Grouping all energy terms on the right as  $\Delta E_{\text{total}}$ , a simplified equation may be written

$$Q - W = \Delta E_{\text{total}} \quad (8)$$

Expressed in this form, Equation 8 is analogous to the usual non-flow expression

$$Q - W = \Delta E$$

**Reversible Steady Flow Work Where Only Mechanical Effects Are Involved.** In visualizing this work effect, imagine a slug of fluid passing through the equipment and separated from those slugs in front and behind by diaphragms rigid enough to serve as pistons. The flow process is then equivalent to a non-flow process having the same  $Q$  and  $\Delta E$  as the flow. As for any non-flow process the work done by the two constant-pressure pistons (diaphragms) is  $\Delta(PV)$ , while between the two pistons a work  $W_{\text{shaft}}$  is done. But the total mechanical work for any reversible non-flow process is  $\int P dV$ . Stated mathematically,

$$\int_{V_1}^{V_2} P dV = W_{\text{shaft}} + \Delta(PV) \quad (9)$$

But the work available for transfer to the surroundings is<sup>1</sup>

$$W_{\text{shaft}} = \int_{V_1}^{V_2} P dV - \Delta(PV) \quad (10)$$

$$W_{\text{shaft}} = - \int_{P_1}^{P_2} V dP \quad (11)$$

<sup>1</sup> Under appropriate circumstances the energies represented by  $(\Delta U^2/2g)$  and  $\Delta X$  are also completely available for doing work on the surroundings.

This term is frequently called the reversible engine, shaft, flow, or pump work of a flow operation, because it represents *net external mechanical energy effect* in any type of expansion or compression equipment operated reversibly.

The mechanical flow (or shaft) work may be graphically indicated and its relation to the non-flow visualized by noting that (Figure 2) the former is the area between the  $P$ - $V$  curve and the  $P$  axis as contrasted

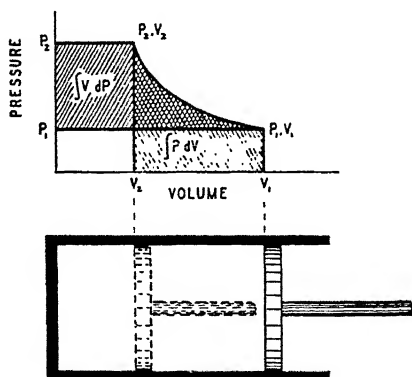


FIG. 2. Graphical Relation between Work Effects in Non-flow and Flow Processes.

with the latter, the area between the  $P$ - $V$  curve and the  $V$  axis. On this same figure the inlet work,  $P_1V_1$ , and the expulsion,  $P_2V_2$ , are also shown. Equating areas in Figure 2, one may readily see that

$$P_1V_1 + \int_{P_1}^{P_2} V dP = P_2V_2 + \int_{V_2}^{V_1} P dV \quad (12)$$

Which simplifies to

$$- \int_{P_1}^{P_2} V dP = \int_{V_1}^{V_2} P dV - \Delta(PV) \quad (13)$$

**Flow Equation for Multiple Streams.** As given, the flow equation is adequate for application to problems involving a single stream. In chemical processes, a multiplicity of streams entering or leaving the process is common. In such cases, each stream must first be treated as a unit, and finally an overall energy balance obtained, in which the total relative energy quantities introduced by each stream are used. Thus, in Figure 3,  $m'$ ,  $m''$ ,  $m'''$  represent the relative masses of each of the streams entering or leaving the apparatus, while  $Q$  and  $W_{\text{shaft}}$  represent the total amount of heat and work transferred as  $m' + m'' \dots$  pass through the apparatus. Consideration of Figure 3 shows clearly the relation between the overall energy balance and the more familiar material balance.

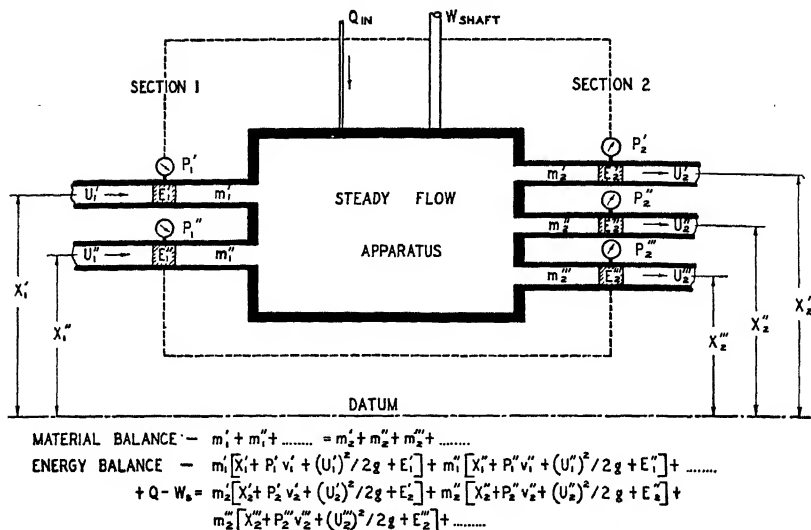


FIG. 3. Overall Energy Balance for Multiple Streams.

**Enthalpy.** The pressure  $P$  and the specific volume  $V$  are obviously determined absolutely by the conditions under which the fluid exists at a given point. It follows that both these, and hence also their product,  $PV$ , are, like  $E$ , point functions; their values depend on the condition of the system at the point in question and are completely independent of the path by which the state was reached. This must be true also of the *sum* of the internal energy and the pressure-volume term. This sum appears not only in the flow equation, but so frequently in thermodynamic calculations that, purely as a matter of convenience, it is usually treated as a unit, described by a single symbol,  $H$ . By definition, therefore,  $H = E + PV$ . The term is so important that it is given a name, but unfortunately, nomenclature is not well standardized. It was originally called total heat, and later heat content, or the heat function. In recent years, however, the word **enthalpy** (*en-thal'-py*) has been introduced to designate this sum. Enthalpy is not heat. While it has the dimensions of energy, and both its terms are energy terms, enthalpy may not be energy. It is merely the sum of  $E$  and  $PV$ .

The zeros of the scales of both pressure and volume are fixed by the physical character of these entities, but since this is not true of internal energy, it is also not true of enthalpy. With enthalpy, as with internal energy, usually differences only are dealt with *i.e.*,  $\Delta H = \Delta E + \Delta(PV)$ .

In many flow problems not all the energy effects corresponding to those given in Equation 5 appear. Some cases of interest and importance are given in Table I.

TABLE I  
IMPORTANT CASES OF FLOW EQUATION

Condition of Flow	Form of Flow Equation	Example of Use
1. Adiabatic, with external work effect	$-W_{\text{shaft}} = \Delta H + \Delta X + \Delta \frac{U^2}{2g}$	General flow of fluids
2. Adiabatic, with external work effect. Velocity and potential energy effects negligible	$-W_{\text{shaft}} = \Delta H$	Adiabatic steam engine and turbine
3. Adiabatic, no external work effect, potential energy effects negligible	$-\Delta H = \Delta \frac{U^2}{2g}$	Adiabatic flow nozzle
4. Adiabatic, no external work effect, velocity and potential energy effects negligible (The Joule-Thomson expansion)	$\Delta H = 0$	Joule-Thomson expansion, adiabatic flow through a line of high resistance
5. No external work effects, velocity and potential energy effects negligible	$Q = \Delta H$	Feed-water heaters and in general all types of flow heaters or coolers

### SUMMARY

1. The experimentally determined fact that energy can neither be created nor destroyed was emphasized. The characteristics of internal energy were presented.

2. Two important mathematical expressions were developed for the first law of thermodynamics

(1) For non-flow processes:

$$Q - W = \Delta E$$

(2) For flow processes (basis: unit mass):

$$Q - W_{\text{shaft}} = \Delta E + \Delta(PV) + \Delta \frac{U^2}{2g} + \Delta X$$

3. For reversible flow processes where only mechanical effects are involved

$$W_{\text{shaft}} = - \int_{P_1}^{P_2} V dP$$

4. By definition the sum  $E + PV$  is called the enthalpy. It is a point function.



## NOTATION FOR CHAPTER II

$A$	Area (of piston)
$E$	Internal energy
$H$	Enthalpy = $E + PV$
$L$	Distance (which piston moves)
$P$	Absolute pressure
$Q$	Heat withdrawn from the surroundings (added to system)
$U$	Average velocity
$V$	Volume
$W$	Work done by system on the surroundings
$X$	Height above datum plane
$d$	Differential or infinitesimal amount
$g$	Gravitational acceleration constant = 32.2 ft./sec.) <sup>2</sup>
$m$	mass

*Greek letters*

$\Delta$  Final value — Initial value

*Superscripts*

', ', ''' refer to different streams (for multiple stream steady flow)

## PROBLEMS

1. Write the appropriate simplified energy expressions for the following changes. In each case the amount of material to be used as a basis of calculation is 1 lb. and the initial condition is 100 lb./sq. in. abs. and 370°F.

(a) The substance, enclosed in a cylinder fitted with a movable frictionless piston, is allowed to expand at constant pressure until its temperature has risen to 550°F.

(b) The substance, enclosed in a cylinder fitted with a movable frictionless piston, is kept at constant volume until the temperature has fallen to 250°F.

(c) The substance, enclosed in a cylinder fitted with a movable frictionless piston, is compressed adiabatically until its temperature has risen to 550°F.

(d) The substance, enclosed in a cylinder fitted with a movable frictionless piston, is compressed at constant temperature until the pressure has risen to 200 lb./sq. in. abs.

(e) The substance is enclosed in a container which is connected to a second evacuated container of the same volume as the first, there being a closed valve between the two containers. The final condition is reached by opening the valve and allowing the pressures and temperatures to equalize adiabatically.

2. Write the simplified energy expressions for the following changes:

(a) A fluid flows steadily through a poorly designed coil in which it is heated from 70° to 250°F. The pressure at coil inlet is 120 lb./sq. in. abs., and at coil outlet is 70 lb./sq. in. The coil is of uniform cross section, and the fluid enters with a velocity of 2 ft./sec.

(b) A fluid is expanded through a well-designed adiabatic nozzle from a pressure of 200 lb./sq. in. abs. and a temperature of 650°F. to a pressure of 40 lb./sq. in. abs. and a temperature of 350°F. The fluid enters the nozzle with a velocity of 25 ft./sec.

(c) A turbine directly connected to an electric generator operates adiabatically. The working fluid enters the turbine at 200 lb./sq. in. abs. and 640°F. It leaves the turbine at 40 lb./sq. in. abs. and at a temperature of 350°F. Entrance and exit velocities are negligible.

(d) The fluid leaving the nozzle of part (b) is brought to rest by passing through the blades of an adiabatic turbine rotor and leaves the blades at 40 lb./sq. in. abs. and at 400°F.

(e) A fluid is allowed to flow through a cracked (slightly opened) valve from a region where its pressure is 200 lb./sq. in. abs., and 670°F., to a region where its pressure is 40 lb./sq. in. abs., the whole operation being adiabatic.

3. A cylinder, closed at one end, is fitted with a movable piston. Originally the cylinder contains 1.2 cu. ft. of gas at 7.3 atm. pressure. If the pressure be reduced to 1 atm., calculate the work done by the gas on the piston face, assuming the following relationships to hold: (a)  $p v = \text{a constant}$ : (b)  $p v^{1.3} = \text{constant}$ , (c)  $v = \text{a constant}$ .

4. To what final velocities could the work done by the gas in parts (a), (b), and (c) of Problem 3 accelerate a body having a weight of 27 lb., if the body starts from rest? If it has an initial velocity of 25 ft./sec.?

5. Through what increase in vertical height could the body of Problem 4 have been raised by the same work expenditures?

6. If the works done by the gas in Problem 3 are used to charge a 6-volt storage battery at a rate of 6 amperes, and with 100 per cent efficiency, how long will the charging continue?

7. Plot the  $p-v$  relations for each of the changes of Problem 3 on rectangular coordinate paper. Plot the logarithms of  $p$  versus the logarithms of  $v$  on rectangular paper.

8. Assuming that there exists a constant frictional force equivalent to a pressure of 10 lb./sq. in. on the face of the piston in Problem 3, what work output may actually be obtained from the outer end of the piston for each of the three changes of that problem?

9. If the changes of Problem 3 were reversed, *i.e.*, the pressure of the gas returned to 7.3 atm., along the same path, and if the frictional conditions were as in Problem 8, what work input to the outer end of the piston would be required?

## CHAPTER III

### EQUILIBRIUM AND THE PHASE RULE

Before proceeding with the more technical aspects of our subject, several terms of frequent utility will not only be defined but also explained in their broader meanings. In a very real sense this chapter is a review of familiar but often not too well-formulated ideas. The material treated may well be divided into two major parts: (1) equilibrium; (2) the phase rule.

#### EQUILIBRIUM

The concept of a *state or condition of equilibrium* is fundamental. Any system is said to be in equilibrium when all potentials acting on it are balanced — a system in equilibrium undergoes no perceptible progressive change with time. Often the rate of change is exceedingly slow, and in chemical systems it is common practice to test for an equilibrium condition by approaching the desired state first from one direction, then from the other. In this way the experimental difficulties due to slow reaction rate are minimized.

The idea of no perceptible progressive change with time does not preclude random changes which ordinarily are not detected. In a body of gas at uniform temperature and pressure throughout, the molecules are in random motion, and from instant to instant there must be imperceptible temperature variations from one part of the gas to the other, yet these unmeasurable effects may be neglected in connection with a discussion of equilibrium.

It is not necessary that like potentials be balanced against each other. The balancing of a gravitational force by a magnetic is familiar to all. It is possible to balance a chemical potential by an electrical or mechanical force. This is illustrated by a system composed of metallic zinc in very dilute sulfuric acid. At ordinary temperatures and pressures the zinc will be consumed, liberating hydrogen gas and forming zinc sulfate. An unbalanced chemical potential is causing the change. If this system, always at the same temperature, be subjected to increasing, externally applied, hydrogen pressure (Figure 1), eventually a pressure will be reached above which the zinc is no longer consumed by the acid — a condition such that a mechanical force is balancing a chemical potential. Considering once more the zinc and acid, at room tempera-

ture and atmospheric pressure, the tendency for the two to interact may be balanced and the reaction prevented by placing the proper electrical potential on the system. This might be accomplished by dipping a chemically inert carbon rod into the acid and connecting it to the correct side of a properly chosen external source of electricity. The metallic zinc in contact with the acid will serve as the other connection with the external circuit. In this case a chemical potential is balanced by an electrical force.

At equilibrium a system is not necessarily in a state of complete rest. Our ordinary idea of chemical equilibrium is that of two opposing reactions, each proceeding at such a rate that the products formed by the one are constantly consumed by the other so that there is no *net* change in the quantities or kinds of materials in the system.

Any system not in equilibrium tends to attain this state, although the rate of approach may be exceedingly slow. The universal tendency to attain equilibrium — a balance of potentials — is often stated by saying, "If a spontaneous reaction is possible, it will occur." This is a fact, the result of almost countless experiments. It is an expected consequence of the concept of potential.

**Complete Equilibrium.** Often a system is at equilibrium relative to one datum but not to another. A ball resting on a table edge is certainly in equilibrium (relative to the table, if you wish), yet the slightest push will send it falling to the floor where, after it comes to rest, it is once more in equilibrium, this time relative to the floor. Indeed, all actual equilibria would seem to be relative. This is not a new point of view. Previously, internal energy and enthalpy, for practical purposes, were considered as relative or measured above some datum. Similarly most equilibria must be considered relative rather than absolute.

A system may be in equilibrium in some respects but not in all. In a gaseous mixture of hydrogen and oxygen at room temperature and atmospheric pressure throughout, thermal and mechanical equilibrium prevail, yet the gases are not in chemical equilibrium. An electric spark, a glowing particle, or a small amount of the proper catalyst will cause a rapid and usually explosive chemical reaction resulting in a

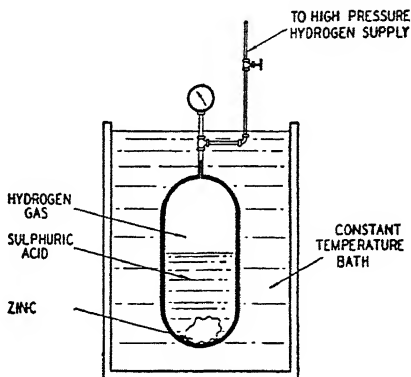


FIG. 1. Balance of Chemical Potential by Gas Pressure.

condition of chemical equilibrium with practically nothing but water remaining.

**Types of Equilibria.** The student of mechanics distinguishes between dynamic and static equilibria, the former exemplified by the spinning top or the rotating flywheel, the latter by a body at rest. Usually three types of static equilibria are recognized: stable, unstable, and neutral. A cone resting on its base is in *stable*, balanced on its apex it is in *unstable*, and resting on its side it is in *neutral* equilibrium. The idea of reversible chemical reactions bears a close analogy to mechanical dynamic equilibrium, while the common metastable conditions, such as experienced with supercooled liquids, are comparable to the mechanical unstable equilibrium. In much the same way that the cone, on its apex, remains balanced if heated, carefully raised or lowered vertically, electrically charged, or even magnetized, so the supercooled liquid may be reheated and cooled and in many cases violently agitated without causing separation of solid. To send the balanced cone crashing to its side it is only necessary to subject it to an unbalanced mechanical force — push it sideways. To cause precipitation of a crystal crop from the supercooled liquid it is only necessary to add a single crystal of the material — to subject the solution to unbalanced forces existing at the crystal faces.

**Friction.** In mechanical systems friction is one type of force the existence of which must be assumed to explain certain conditions. *Static friction* balances a stationary block on an inclined plane, and it is *dynamic friction* which eventually brings the spinning top to rest. To explain chemical reactions which proceed exceedingly slowly, such as the formation of water from oxygen and hydrogen at room temperature and without a catalyst, something analogous to “friction forces” is sometimes assumed. This analogy is open to criticism and need not especially concern us as we shall usually be interested in determining whether a given reaction will go in the absence of such “frictional effects.”

Many workers in thermodynamics distinguish between those passive forces which prevent change, such as the static friction of mechanics, and forces which only retard change, such as viscosity in a moving fluid. Truly frictional forces prevent certain changes whereas “viscous forces” retard change.

**Chemical Potential.** The idea of mechanical, electrical, thermal, and similar forces is familiar. To a limited extent these are understood, and the methods for detecting and measuring them are common knowledge to many engineers. It is not so easy to visualize the potential effect which determines whether or not chemical changes can occur. The long search for the chemical potential or driving force for chemical

reaction is an interesting chapter in the history of science. More than anyone else, J. Willard Gibbs (1839–1903) is responsible for the correct thermodynamic interpretation of the problem, but even today a clear understanding of the mechanism of chemical reaction is lacking.

The one test for equilibrium, where chemical reactions are involved, as in the more simple cases previously mentioned, is to determine whether or not all potentials are balanced. A discussion of methods for determining chemical potentials must be postponed until a later chapter.

**Equilibrium and Reversibility.** It is usually convenient to consider a **reversible process** as one occurring in such a way that the system is never more than differentially removed from an **equilibrium state**. The path traced by a reversible process may be thought of as the locus of a series of equilibrium states, the last of which may be far different from the first, as it is when steam expands reversibly through a carefully insulated nozzle. However, the final state of a system undergoing a reversible process *may differ* but differentially from the first, as in the transfer of a finite amount of heat from a body at constant temperature  $T$  to one at constant temperature  $T + dT$ .

The "equilibrium evaporation" of a liquid is often postulated. Thus it is assumed that water, in equilibrium contact with its vapor, can be evaporated, the temperature and pressure remaining constant, and, irrespective of the relative amounts of liquid and vapor, equilibrium is always maintained. This would seem to be a case, where, although potentials are always balanced, a change does occur. Such a change cannot actually be carried out. Theoretically, it would require that the heat added for evaporation be at least differentially higher in temperature than the water-vapor mixture itself, and actually even in carefully conducted experiments a measurable difference in temperature always exists. Such an evaporation for the theoretical case is really a reversible process in which the system, as in all reversible processes, is never more than differentially removed from an equilibrium state but where, in addition, irrespective of how far the process proceeds, the system is never more than differentially removed from the initial condition of equilibrium.

### THE PHASE RULE

Although the phase rule may be familiar, it will be summarized here, both as a matter of reference and to ensure that no uncertainty exists regarding the nomenclature to be employed.

Matter exists in three forms: solid, liquid, and gaseous (or vapor). This classification does not include the colloidal form or the so-called liquid crystals. So far, treatment of these by the generalizations of the phase rule has not been completely satisfactory. Amorphous solids should probably be classified as supercooled liquids.

**Phase.** A quantity of matter is said to be homogeneous when no differences in physical or chemical properties can be detected throughout its mass. Any quantity of matter, homogeneous throughout, is called a **phase**. To be homogeneous, a phase need not be continuous. Thus, snowflakes or raindrops in the air, or undissolved salt crystals dispersed in a saturated solution, constitute a single phase as truly as the air itself or the solution in which the crystals are suspended. Phases can interact with each other and can also exist under conditions of interphase equilibrium.

**Necessary Conditions.** The phase rule applies only to conditions of equilibrium both within a given phase and between the phases of a system. It may, however, be applied to one group of possible reactions, others being ignored, *provided that the latter do not occur to a significant extent under the conditions existing in the system*. From the viewpoint of the phase rule this is equivalent to assuming that the second set of reactions cannot occur at all. For example, the phase rule could be applied to the equilibrium involving solution of a gaseous hydrogen-oxygen mixture in liquid water, despite the fact that the gases themselves tend to combine chemically to form water, and in this respect are not in equilibrium. This last effect can be ignored at normal temperature, in the absence of a catalyst, because, under these conditions, the reaction rate is negligible.

The use of the phase rule always requires judgment and intelligence. Not only the particular system but also the kind of change to which it is to be subjected must be clearly stated. In the case of the system  $H_2$ ,  $O_2$ , and water just mentioned, one must know whether the solubilities of the gases in water are to be discussed or the reaction of  $H_2$  and  $O_2$  to form water.

**Components.** The components of a system are the smallest number of pure chemical compounds or constituents needed to make up any and all phases by addition or subtraction of these only. Subtraction is rarely necessary. Those materials which could be mixed actually to produce any and all phases present might be chosen as components. Sometimes the elements entering into the reaction are a satisfactory choice. Even in the same system, choice of components is sometimes optional. Thus, in the crystallization of  $NaHCO_3$  from a solution of  $Na_2CO_3$  by means of  $CO_2$  gas,  $Na_2CO_3$ ,  $H_2O$ ,  $CO_2$ , or  $Na_2O$ ,  $CO_2$ ,  $H_2O$  may be selected.

To choose the components correctly requires a thorough knowledge of the chemical characteristics of the substances involved — so thorough, unfortunately, that one is sometimes prone to feel there is but little left to be learned by any such generalization as the phase rule. Actually,

this rule is more useful as a method of systemization than as an aid in prediction.

**Extensive and Intensive Variables.** The properties of a system may be classified in two major categories: those proportional to the total amount of matter in the system, and those *completely independent* of the relative quantities of matter in the various phases. The first group constitutes the *extensive*, the second, the *intensive*, properties. Examples of extensive properties are weight, mass, the total volume of the system (or of any of its phases), total internal energy, total enthalpy, and dimensions in general. Examples of intensive properties are pressure (including partial pressures), temperature, concentrations, densities, refractive indices, and all such properties as specific volume, thermal conductivities, electrical conductivities.

**Variance.** The phase rule deals only with intensive properties. Any truly intensive property is called a phase-rule **variable**. In any system the number of independent phase-rule variables is called the **variance**. The variance is the number of intensive state properties of each phase which must be fixed to fix completely all intensive properties of all phases. Systems of but one such variable are called monovariant; those of two, divariant; those of three, trivariant.

As a result of observations on a series of familiar systems, excluding gravitational, electrical, surface, and similar effects, the following relation may be formulated:

$$P + V = C + 2$$

where

**P** = number of phases.

**V** = variance.

**C** = number of components.

This is the phase rule. Though here the relation is established empirically, its fundamental nature will be developed in a later chapter.

Certain properties are independent of the quantity of matter but not of the distribution of this matter between phases in a multiphase system. A mixture of water vapor and liquid water in equilibrium is monovariant; *i.e.*, fixing the pressure, the temperature, the specific volume of the liquid or of the vapor, or any other single and truly intensive variable will determine the system. All these are independent of the quantity of matter. The fraction of the total material present as either water vapor or liquid water is also independent of the actual total amount present, but not of its distribution between phases. This ratio of water vapor to liquid water might be called an intensive variable, but *it is not a phase-rule variable*, because specifying it will not fix a system composed of water vapor and liquid water. It is well to avoid, as far as possible, variables of this mixed type. For most systems the phase-rule variables are pressure,



temperature, and the composition of each phase. The phase rule indicates nothing as to the relative masses of the phases.

The volume per unit mass of matter might be termed the specific volume of the mixture, but it seems more logical to speak of such properties as specific properties only where they may be applied to a single phase. Mention will be made of the specific volume of water or steam but not of the "specific volume" of wet steam. The specific volumes are true phase-rule variables; the volumes of mixtures per unit mass of mixture are not phase-rule variables.

**Systems of Not More than Two Independent Variables.** It might appear that often in thermodynamic calculations there would be several independent variables with the attendant mathematical difficulties.

To facilitate calculation, engineering problems are usually formulated with but two independent variables. To this end small changes due to gravitational, electrical, magnetic, or surface effects are usually neglected, although colloidal solutions constitute a situation where surface effects cannot be neglected. In the ultimate analysis even the effect of gravity on concentrations from the bottom to the top of a tank containing an otherwise uniform solution must be considered.

### PROBLEMS

For each of the following systems give the components and the variance:

1. Ice and water in equilibrium at 1 atm.
2. The system formed by allowing 1 mol of ammonia gas and 1 mol of HCl gas to come to equilibrium at 400°C. and 1 atm.
3. The system made up of the reacting mass and its gas phase in a Mannheim furnace producing hydrochloric acid by the interaction of sodium bisulfate ( $\text{NaHSO}_4$ ) and sodium chloride ( $\text{NaCl}$ ).
4. A mixture of alcohol and water in equilibrium with its vapor.
5. The gaseous mixture undergoing conversion in the vanadium oxide catalyst chamber of a plant making sulfuric acid by the contact process.
6. A gas oil (mixture of  $n$  mutually soluble hydrocarbons) under a pressure and temperature such that the system is (a) part liquid and part vapor, (b) 50 mol per cent vapor and 50 mol per cent liquid.
7. A 20 per cent by weight solution of sodium hydroxide in water at 25°C. and 1 atm. pressure.

## CHAPTER IV

### PHASE RELATIONS

This section is a summary of experimental results — merely a description of what happens when energy is added to matter. Our study will be considerably simplified and not greatly limited if attention is directed to changes in those variables of primary importance. These are pressure, temperature, volume, and composition (often expressed in percentage of the various kinds of matter present, irrespective of forms). Throughout this discussion, equilibrium and no chemical change (unless otherwise stated) will be assumed.

**General Considerations.** Experiments indicate that any kind of matter at a finite pressure but high enough temperature will be gaseous. This presupposes the absence of chemical decomposition, which often takes place at temperatures lower than those necessary for complete or even partial gasification. Thus at atmospheric pressure glycerine decomposes before completely vaporizing and cellulose chars before even melting.

As the temperature is lowered, the pressure remaining constant, usually liquid formation is evident, and, after a sufficient amount of energy has been lost from the material under observation, the gas phase will have been entirely converted to liquid. Further loss of energy will eventually result in complete solidification at lowered temperatures.

At properly chosen pressures substances pass directly from gas to solid form without first becoming liquid. Under ordinary conditions iodine behaves in this way. The reverse change, formation of a gas from a solid, is called sublimation.

Sometimes it is difficult to decide whether a quantity of matter is in the liquid or gaseous condition. A liquid not only assumes the shape of the cavity into which it is poured but, unlike a gas, has a definite volume in the sense that if placed in too large a space it will not entirely fill it. A liquid will also "splash" if violently disturbed. A solid cannot entirely fill a space larger than itself, but unlike either a liquid or a gas its shape will not conform exactly to that of the container.

**Single-Component Systems.** The phase rule correlates the number of independent truly intensive variables with the number of possible coexistent phases. From this the former cannot exceed two nor can the latter be greater than three in single-component systems.

It must not be inferred from this that a one-component system is limited to three different phases. Thus water may exist as gas, liquid, and several different forms of ice. For some substances at least six different phases are known.

Water is a familiar example of this class. In many respects its changes are representative of all single-component systems. With one kind of matter present, composition cannot be a variable. Since pressures and temperatures can be experimentally measured more readily and with a higher degree of accuracy than volumes, attention will be directed to the first two. These may be thought of as the independent variables.

To aid in visualizing, let a quantity of water be placed in a transparent cylinder fitted with a light, perfectly fitting frictionless piston. The water may be subjected to any desired pressure by weighting the piston. Place the apparatus in a thermostat so that, as the necessary amounts of energy are absorbed or rejected by the cylinder contents, the tem-

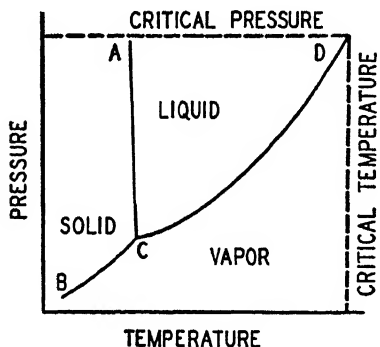


FIG. 1. Phase Diagram for Water.

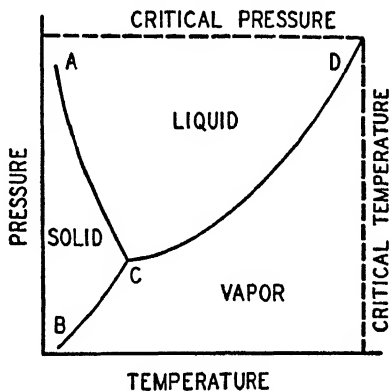


FIG. 2. Phase Diagram for Carbon Dioxide.

perature may be held constant at different levels. With equilibrium maintained, proceed to vary the pressure isothermally. If the pressures and temperatures at which phase boundaries form are noted, a *phase diagram* similar to Figures 1 or 2 may be constructed.

**Definitions.** The curve  $C-D$  is the **vapor-pressure** curve, and its terminus at  $D$  is called the **critical point**. The **critical temperature**, that corresponding to point  $D$ , is the highest temperature at which the material can be made to assume the characteristics of a liquid irrespective of the pressure applied. The pressure corresponding to the point  $D$  is the **critical pressure**.

That point  $C$  on a pressure-temperature diagram for a single component where three coexisting phases are in equilibrium is called a

**triple point.** Even for one-component systems more than one triple point is possible. Thus, according to Riecke,<sup>1</sup> for  $N$  different phases the number of possible triple points is  $\frac{N(N-1)(N-2)}{1 \cdot 2 \cdot 3}$ , and the possible two-phase monovariant systems are  $\frac{N(N-1)}{1 \cdot 2}$

Vapor in equilibrium with its liquid (possible along  $C-D$ )<sup>2</sup> is called **saturated**; at higher than the equilibrium temperature corresponding to any chosen pressure, **superheated**.

For any temperature below the critical a **subcooled liquid** is one at a pressure exceeding its corresponding saturation pressure.

**Pressure-Temperature-Volume Relations.** In the previous experiments, pressures and temperatures were measured. Had a record also been kept of the total volume occupied by the substance, a diagram similar to Figure 3 could now be drawn. This clearly shows the large volume change, at any constant pressure and temperature less than the critical, due to vaporization. Solid phase regions may readily be located.

Even for simple single-component systems sufficient data for drawing a complete phase diagram are practically never available. Fortunately for engineering purposes a partial diagram covering the important conditions is sufficient. For multicomponent systems data are even less complete. All figures in this chapter are but sections. More complete diagrams are found in treatises on heterogeneous equilibria.

**Monovariant Changes.** Constant-pressure vaporizations, fusions, or sublimations are of importance in thermodynamic calculation. During these there is absorption of energy (heat) without change in temperature. Such isothermal effects are known as latent heats, as contrasted to sensible heat effects wherein a temperature change does occur.

**Critical Phenomena.** As the critical point is approached, interesting changes occur in the liquid and vapor in equilibrium contact. If the material is contained in a transparent tube, as was suggested for conducting experiments of this type, the meniscus, separating liquid and vapor, flattens as the critical condition is neared. Just at the critical

<sup>1</sup> *Z. physik. Chem.*, 6, 272 (1890).

<sup>2</sup> It is possible to change the vapor pressure of a pure liquid held at constant temperature by changing the pressure on it. Except for large changes in total pressure, the change in vapor pressure with pressure is small and need not concern us at this time. Because of surface energy effects, the vapor pressure of small droplets differs from that of a body of the same liquid under otherwise similar conditions. Unless the liquid is in highly dispersed state, this effect is negligible in engineering work. The effect must often be considered in handling mists and fogs.

the meniscus becomes indistinct and a region of haze takes its place. No distinction can be observed between liquid and vapor. Indeed, careful measurements made on the characteristics of the two, as the critical point is approached, show that they differ less and less, finally losing their individual identities. Figure 4, based on data from the "International Critical Tables," Vol. 3, page 238, is a plot of liquid

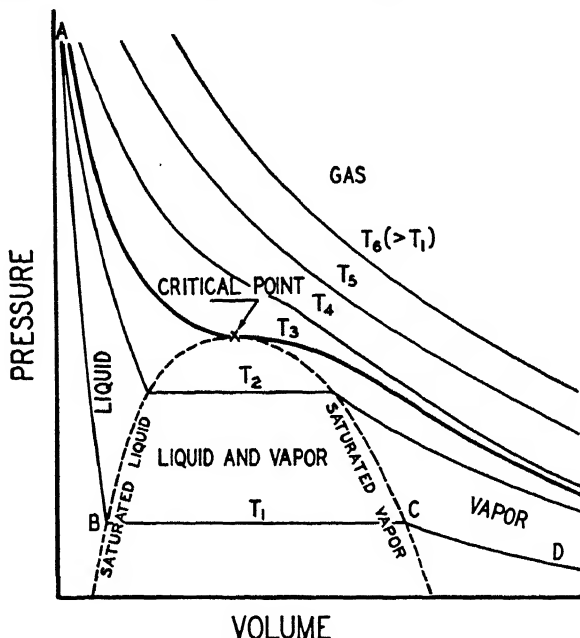


FIG. 3. Isotherms on Pressure-Volume Plane.

and vapor densities versus temperature for ethyl alcohol. Cailletet and Mathias pointed out that on such a plot the averages of the liquid and vapor densities lie on a line, almost straight and passing through the critical point. This rule seems to be true for all substances and is of some value in locating the critical density. Unfortunately the curvature is greatest near the critical.

**Binary Mixtures with Components of Complete Mutual Solubility.** The previous discussion was limited to single pure materials. Like these, at sufficiently low temperatures all mixtures are solids. Since most elementary textbooks on physical chemistry discuss the solid state in some detail, consideration here will be limited primarily to the liquid and vapor state and more particularly to the neighborhood of the critical.

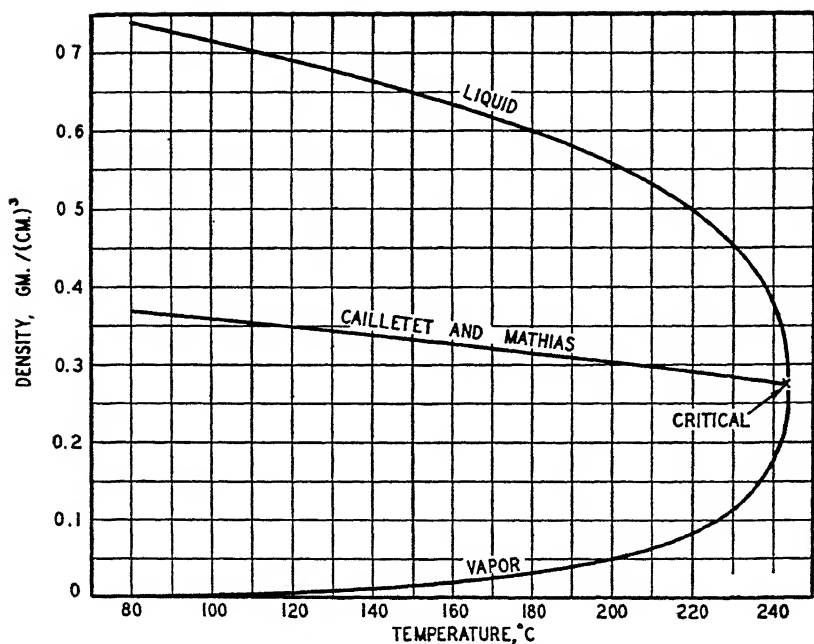


FIG. 4. Density of Saturated Vapor and Liquid of Ethyl Alcohol. Based on data from the "International Critical Tables," Vol. 3, p. 238.

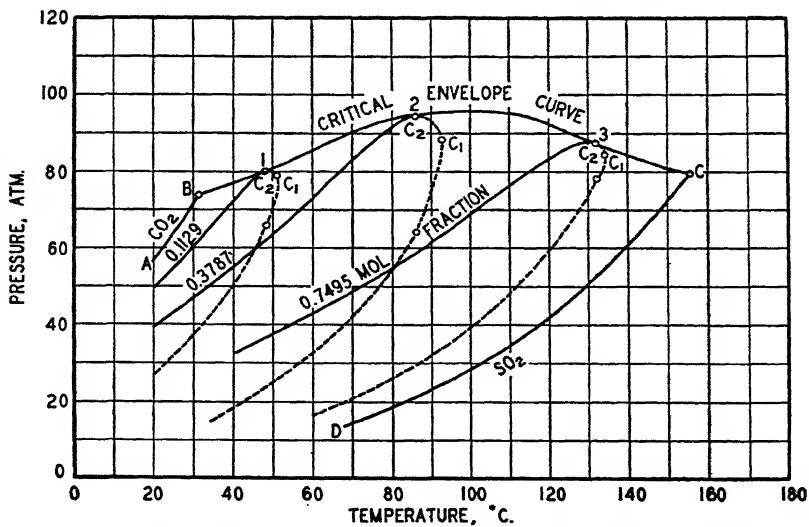


FIG. 5. Pressure-Temperature Relations at Constant Composition for Mixtures of  $\text{CO}_2$  and  $\text{SO}_2$ . (37)

If the cylinder and piston experiment is repeated with a binary mixture the constituents of which are mutually soluble in all proportions, more complicated results are obtained. Here, in addition to the variables pressure, temperature, and volume, must be added that of composition. The experimental data on mixtures are often presented as a series of loop curves, as in Figure 5.<sup>1</sup>

This figure gives the  $P$ - $T$  relations for a mixture of  $\text{CO}_2$  and  $\text{SO}_2$ . The line  $A$ - $B$  is the upper end of the vapor pressure curve for  $\text{CO}_2$ ;  $D$ - $C$  is a similar curve for  $\text{SO}_2$ . The solid line connecting points  $B$  and  $C$ , marked "Critical envelope curve," is the locus of the so-called **second critical points** for all mixtures of  $\text{SO}_2$  and  $\text{CO}_2$ . At these second critical points ( $C_2$ ) there is no distinction between liquid and vapor states — the properties of the two are identical. At a few concentrations of  $\text{CO}_2$ , lines somewhat analogous to the vapor-pressure curves for pure substances have been drawn. These are solid and end at points 1, 2, and 3. They represent for the various indicated mixtures the pressures and corresponding temperatures at which vapor formation starts, the *bubble points* as referred to mixtures. The points 1, 2, and 3 are the second criticals for the indicated mixtures. The dotted lines passing through each of these points give, at various pressures, the corresponding temperatures at which the mixtures are just completely vaporized — the *dew-point* curves of the different mixtures. The dew point is so named because it is the temperature at which liquid first forms from a vapor mixture cooled at constant pressure. On a pressure-temperature plot the saturation curve and the vapor-pressure curve, as referred to a single substance, would be superimposed; but for mixtures, as is evident, the bubble-point and the dew-point curves are not.

The terms vapor pressure and saturation refer to pure substances; bubble point and dew point refer to mixtures.

Figure 5 shows that for a mixture of any chosen composition the dew-point curve folds back on itself as one moves away from the second critical ( $C_2$ ), and at the point marked  $C_1$  a place of maximum temperature is reached. For any chosen mixture  $C_1$  marks the highest temperature at which liquid may be condensed from the vapor, and it is called the **first critical temperature**. For pure substances the conditions at the first and second criticals coincide. However, for mixtures, that temperature above which liquid cannot be formed from a given vapor (the first critical) differs from the temperature at which there is no distinction between liquid and vapor (the second critical).

<sup>1</sup> F. Caubet, *Z. physik. Chem.*, **40**, 284 (1902); L. W. T. Cummings, Sc.D. Thesis, Mass. Inst. Tech., 1933.

Reference to Figure 6<sup>1</sup> makes clear the fact that only at the second critical are the characteristics of liquid and vapor the same for mixtures.

Often it is convenient to replot the data of Figure 5, and this has been done in Figures 7, 8, and 9.<sup>2</sup>

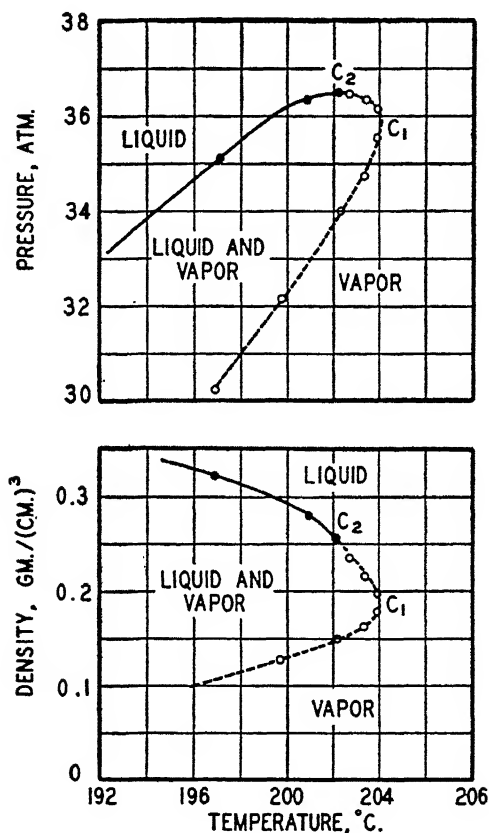


FIG. 6. Pressure-Density-Temperature Relations around the Critical for 48.59 Mol Per cent Butane-Hexane Mixtures.

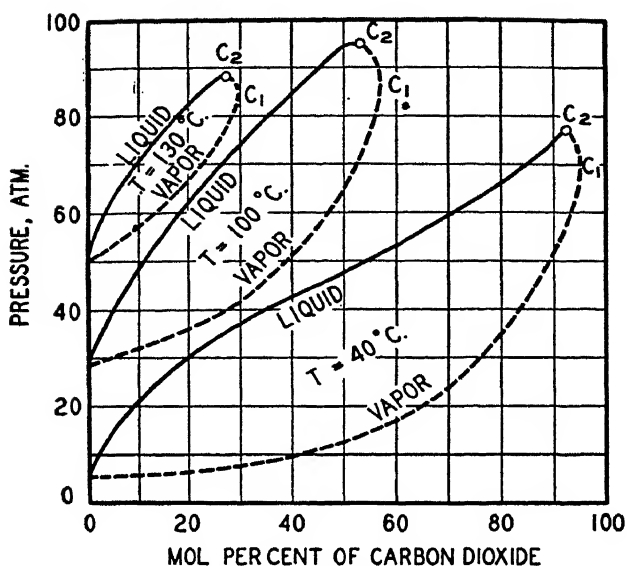
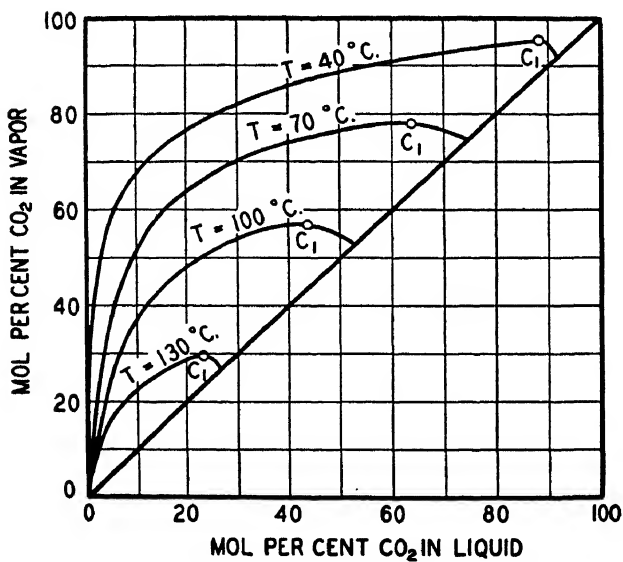
**Retrograde Condensation. First Type.** A little study of Figure 5 will make clear that isothermal compression of a vapor,<sup>3</sup> at any temperature between its first and second criticals, will cause the appearance of a liquid, which, on further compression at constant temperature but

<sup>1</sup> Cummings, Sc.D. Thesis, p. 65.

<sup>2</sup> *Ibid.*, pp. 12-16.

<sup>3</sup> Of course, compression must start at a pressure lower than that corresponding to the dew-point pressure at the temperature in question.



FIG. 7. Pressure-Composition Diagrams for the System  $\text{CO}_2\text{-SO}_2$ .FIG. 8. Vapor-Liquid Equilibria for the System  $\text{CO}_2\text{-SO}_2$ .

necessarily increasing pressure, will evaporate.<sup>1</sup> This phenomenon is called **retrograde condensation**, the word first being used by Kuenen in 1892. Van der Waals in 1881 predicted such a result, and at about the same time Cailletet actually observed retrograde condensation while compressing a mixture of air and carbon dioxide.

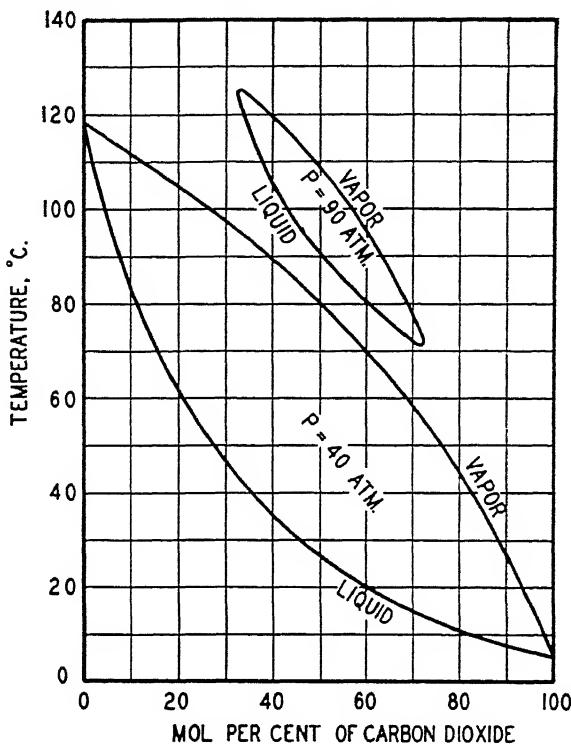


FIG. 9. Temperature-Composition Diagrams for the System  $\text{CO}_2\text{-SO}_2$ .

**Retrograde Condensation. Second Type.** A second type of retrograde condensation is possible. In this the second critical point is at a lower pressure than the first. Furthermore, as the pressure is increased in the neighborhood of the critical, the characteristics of vapor and liquid in contact with each other become more dissimilar rather than more similar (as do mixtures showing retrograde condensation of the first type). In the second type as the pressure is increased at

<sup>1</sup> This is quite the opposite from the action on compressing a pure vapor. For such, compression at any temperature below the critical will cause the formation of liquid as the vapor pressure of the material is attained. Any slight increase in pressure, the temperature remaining constant, will cause the condensation of all the vapor.

constant temperature a material separates less dense than the mixture itself; the amount of this material first increases and then decreases, at last disappearing completely. Duhem<sup>1</sup> called this second type "retrograde vaporization."

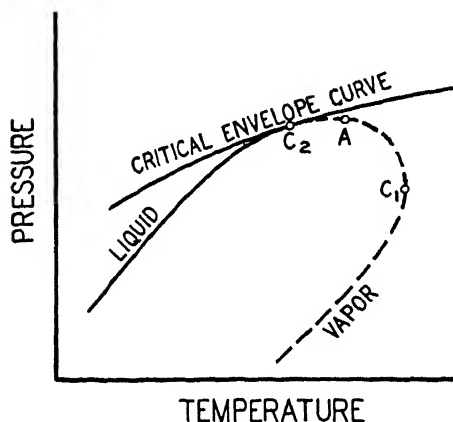


FIG. 10. Pressure-Temperature Diagram for a Composition to Left of Maximum Pressure.

coexistence of a liquid and vapor in contact;  $C_1$  is the highest temperature at which liquid may be condensed from the vapor, the first critical; and  $C_2$  is the point where liquid and vapor have the same characteristics, the second critical. For clarity, on these figures, a curve for but one composition has been sketched, instead of for several as shown on Figure 5. Had a third figure, representing conditions at the maximum of the critical envelope curve, been included, points  $A$  and  $C_2$  would have coincided. In all these  $C_2$  is at a higher pressure than  $C_1$ . All are representative of retrograde condensation of the so-called first type.

**Factors Determining Type of Retrograde Condensation.** As has been pointed out by Kuenen,<sup>2</sup> the pressure-temperature diagrams for mixtures may differ in form from that of Figure 5. The critical curve here goes through a maximum. Figures 10 and 11 represent diagrammatically, to an exaggerated scale, conditions to the left and right of this maximum. On these figures,  $A$  is the point of maximum pressures for the

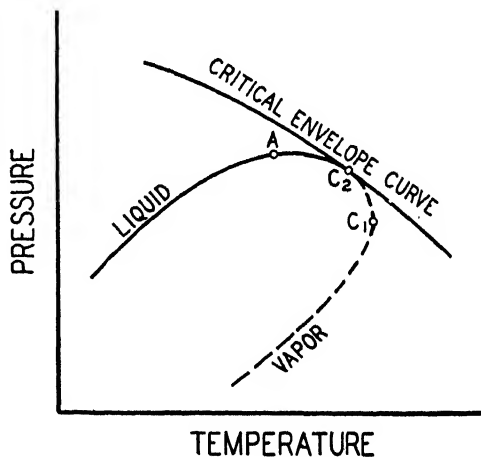


FIG. 11. Pressure-Temperature Diagram for Composition to Right of Maximum Pressure.

<sup>1</sup> *J. Phys. Chem.*, 5, 91 (1901).

<sup>2</sup> "Handbuch der angewandte physikalischen Chemie," Band IV, Leipzig, Johann Barth, 1906.

Where the relative positions of points  $A$ ,  $C_1$ , and  $C_2$ , are as indicated in Figure 12, retrograde condensation of the second type is possible.

**Liquids of Limited Mutual Solubility.** Previous discussion was limited to conditions where but one liquid phase could form. In this section a brief survey will be made of a few two-component systems under a constant pressure so chosen that neither solid nor gas phases can form.

For liquid pairs mutually soluble to a limited extent, there are certain interesting characteristics somewhat paralleling the previously discussed phenomena in the vicinity of the critical.

For any of these a plot may be constructed as indicated in Figure 13. This figure is for some arbitrarily chosen *constant pressure* sufficient to prevent

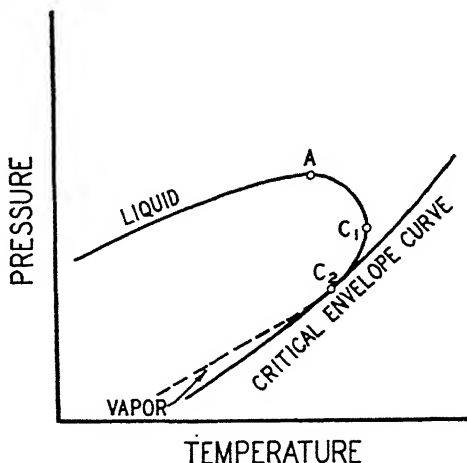


FIG. 12. Pressure-Temperature Diagram for Retrograde Condensation of the Second Type.

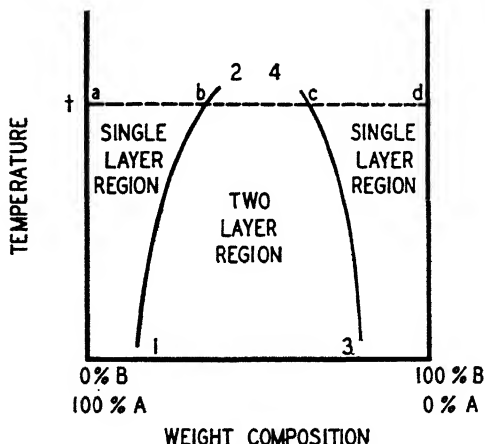


FIG. 13. Temperature-Composition Diagram at Constant Pressure for Partially Miscible Liquids.

vapor formation. Temperatures are plotted as ordinates, while the abscissas are parts by weight per hundred of  $A$  or  $B$  in the *total mixture*. At any temperature  $t$ , on adding  $B$  to  $A$ , the concentrations of the unsaturated solutions formed will be represented by points on the line  $a-b$ . When sufficient  $B$  has been added to give the concentration represented by point  $b$ , the solution will become saturated at  $t$ , and further addition of  $B$  to  $A$  will

cause the mixture to separate into two layers, the compositions of the two layers being given by the concentrations indicated by points  $b$  and

$c$ : a saturated solution of  $B$  in  $A$  represented by  $b$ , and a saturated solution of  $A$  in  $B$  given by point  $c$ . Addition of  $B$  to  $A$  in amounts greater than that indicated by point  $b$  will merely serve to increase the amount of the second layer just formed without changing its concentration. Concentrations to the left of 1-2 or to the right of 3-4 represent, at the various temperatures, those which will yield single-layer systems while all concentrations between 1-2 and 3-4 will give two-layer systems. Lines 1-2 and 3-4 represent the solubilities of  $B$  in  $A$  and  $A$  in  $B$ , respectively.

As temperature is increased, the solubilities of the two materials in each other increase and eventually a temperature  $T_{CM}$  is reached where solutions of any desired concentration may be prepared — the two substances are miscible in all proportions. These conditions are indicated in Figure 14.<sup>1</sup>

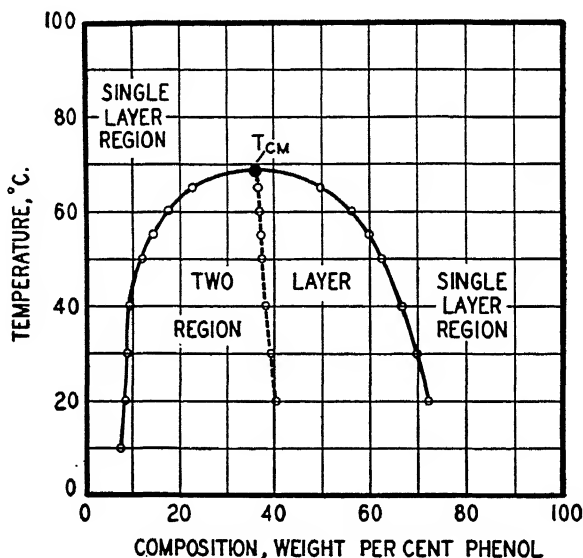


FIG. 14. Temperature-Composition Diagram at Constant Pressure for the System Phenol-Water.

The temperature at which miscibility in all proportions occurs is called the **critical mixing temperature**. As this is attained, phenomena peculiar to the critical are observed — flattening and disappearance of the meniscus between the two layers, appearance of opalescence, and finally identity of the two liquid layers. Moreover, a rule similar to that of Caillietet and Mathias holds. A line practically straight and

<sup>1</sup> Data of Rothmund, *Z. physik. Chem.*, 26, 433 (1898).

passing through the critical mixing temperature is the locus of concentrations at various temperatures, which are the averages of the concentrations (by weight) of the two coexistent layers. This is indicated in Figure 14.

For several pairs of liquids it has been found that solubility, at least over certain ranges, increases with falling rather than with rising temperature and that eventually as temperature falls a point is reached where for any pair miscibility is complete, as indicated in Figure 15.<sup>1</sup>

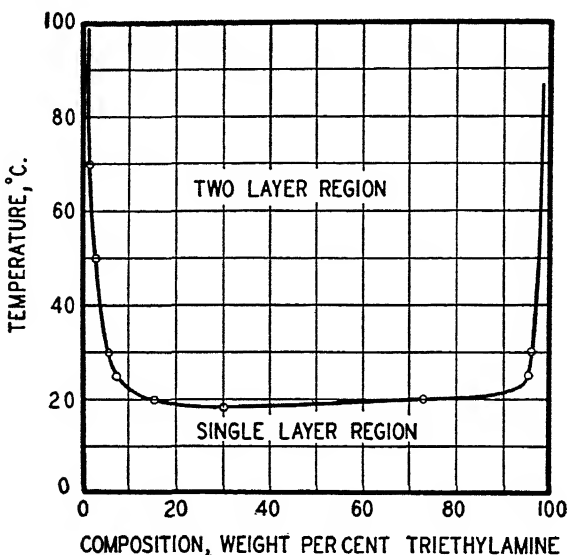


FIG. 15. Temperature-Composition Diagram at Constant Pressure for the System Triethylamine-Water.

This fact, together with those concerning pairs of liquids whose solubilities increase with temperature, has led to the belief that all liquid pairs of the type here discussed possess both a higher and lower critical solubility temperature, and that, if disturbing effects, such as solidification, did not interfere, both limiting temperatures could be determined experimentally. This would result in a solubility diagram consisting of a closed curve within which a two-layer region could exist while all points without would give conditions under which but one layer was possible. Actually this has been found for some pairs of liquids (Figure 16).<sup>2</sup>

<sup>2</sup> Data of Hudson, *Z. physik. Chem.*, 47, 114 (1903), and Tsakalotos, *Bull. soc. chem.*, 5, 397 (1907).

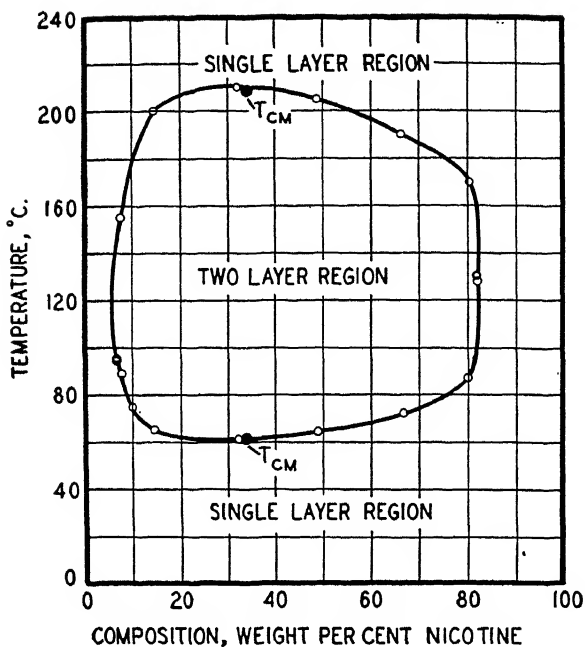


FIG. 16. Temperature-Composition Diagram at Constant Pressure for the System Nicotine-Water.

**Multicomponent Mixtures.** For these systems the relations are similar to those for binary mixtures but as might be expected of a more complicated nature. Often the actual components are not known, the various diagrams being constructed from experimentally determined characteristics of the mixture itself.

## CHAPTER V.

### HEAT CAPACITY AND HEAT OF REACTION

For thermodynamic purposes it is essential to know the energy relations as functions of the independent variables; hence data must be available on the variation of internal energy, or enthalpy (or some equivalent function) with conditions. For homogeneous substances, this information is frequently given in terms of heat capacities. Systems most commonly encountered in chemical engineering work are those of but two independent variables, and discussion will therefore be limited to such cases.

#### HEAT CAPACITY

For a homogeneous body the amount of heat required to cause unit change in any of its characteristics, *e.g.*, temperature, is found experimentally to be a function of: (1) the quantity of material in question, (2) the path followed during the heating, (3) the material under consideration, and (4) the particular conditions under which the material exists.<sup>1</sup>

The heat quantities necessary to cause unit change in one variable while holding some second variable constant will be recognized as the familiar heat capacities,<sup>2</sup> two of which are in common use:

1. **Heat capacity at constant pressure ( $c_p$ )** is defined as the heat necessary to raise a unit amount of a homogeneous material one unit in temperature along a constant-pressure path. If  $c_p$  is a function of temperature, this definition is valid for an average heat capacity over the temperature range in question. Stated mathematically,

$$c_{av.} = \frac{\sum P}{\Delta t} \quad (1)$$

<sup>1</sup> It is understood that the body under discussion undergoes no change in state of aggregation during the processes here in question.

<sup>2</sup> The terms heat capacity and specific heat are often used interchangeably. The heat capacity of a homogeneous quantity of matter is the amount of heat required to cause unit change in some chosen characteristic of the body, usually its temperature. When a unit quantity of matter is under discussion the corresponding heat capacity might be termed the specific heat capacity, but usually this distinction is not made. A specific heat is the ratio of the heat capacity of a body to the heat capacity of the same quantity of water at some arbitrarily chosen condition.



The instantaneous or true heat capacity at any temperature level is given by the differential expression

$$c_p = \frac{dQ_p}{dt} \quad (2)$$

From a consideration of the first law:

$$c_p = \left( \frac{\partial E}{\partial t} \right)_p + P \left( \frac{\partial V}{\partial t} \right)_p = \left( \frac{\partial H}{\partial t} \right)_p \quad (3)$$

2. **Heat capacity at constant volume** ( $c_v$ ) is the heat necessary to raise unit amount of material one unit in temperature along a constant-volume path.

$$c_{v_{av.}} = \frac{Q_v}{\Delta t} \quad (4)$$

and

$$c_v = \frac{dQ_v}{dt} \quad (5)$$

$$c_v = \left( \frac{\partial E}{\partial t} \right)_v \quad (6)$$

In addition to the two already mentioned there are many other heat capacities; *e.g.*, the heat necessary to cause unit change in pressure in unit amount of material, the temperature remaining constant; and that required to cause unit change in volume, the temperature remaining constant, *i.e.*,  $dQ_T/dP$  and  $dQ_T/dV$ . Similarly,  $dQ_V/dP$  and  $dQ_P/dV$  are heat capacities. These last four "heat capacities" find but little application in engineering work although they are of importance in classical thermodynamics.

In both the English and the metric systems the unit amount of heat is defined as that necessary to raise a unit amount of water one degree in temperature at a constant pressure of one atmosphere, although there is no agreement as to the temperature level at which the rise occurs. It should be noted that the heat capacities of materials in general are numerically equal to *specific heats*. These are defined as the ratio of the amount of heat necessary to cause unit change in temperature of the material in question as compared with the amount of heat necessary to raise unit amount of water one unit on the temperature scale. The specific heats are dimensionless ratios, numerically the same in any consistent system of units, whereas the heat capacities have the dimensions of energy divided by temperature.

There are certain general expressions connecting the various heat capacities. It has already been pointed out:

$$c_v = \left( \frac{\partial E}{\partial T} \right)_V$$

and

$$c_p = \left( \frac{\partial E}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P$$

In the systems under discussion  $E$  is a function of but two independent variables. Choosing as these  $T$  and  $V$ ,

$$E = f(T, V) \quad (7)$$

The total differential of  $E$  is:

$$dE = \left( \frac{\partial E}{\partial T} \right)_V dT + \left( \frac{\partial E}{\partial V} \right)_T dV \quad (8)$$

and

$$\left( \frac{\partial E}{\partial T} \right)_P = \left( \frac{\partial E}{\partial T} \right)_V + \left( \frac{\partial E}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P \quad (9)$$

From this it follows that

$$c_p - c_v = \left[ P + \left( \frac{\partial E}{\partial V} \right)_T \right] \left( \frac{\partial V}{\partial T} \right)_P \quad (10)$$

Another general relationship known as the Reech theorem is of interest:

$$\frac{c_p}{c_v} = \frac{\left( \frac{\partial P}{\partial V} \right)_{Q=0}}{\left( \frac{\partial P}{\partial V} \right)_\pi} \quad (11)$$

Here the subscript  $Q = 0$  indicates a reversible adiabatic change. None of these last expressions involves more than the first law expression, the definitions of  $c_p$  and  $c_v$  previously given, and a knowledge of elementary calculus. They represent a few of the almost countless relationships to be obtained by judicious "mathematical juggling." Of the various relationships which can be derived, but comparatively few are of frequent importance in engineering work.

The determination of heat capacities is really a problem of physics and will not be discussed at any length in this book, but it should be emphasized that they are never determined directly but are calculated as a function of temperature from measurements such as change in enthalpy or internal energy, made by the usual calorimetric methods.

**Estimation of Heat Capacities.** The determination of heat capacities over a range of temperature is time-consuming and expensive. For many materials, data are incomplete or lacking entirely. It is therefore desirable to have methods of estimating the heat capacities of various materials, and some of engineering importance are given here.

**Law of Dulong and Petit for Solid Elements.** According to the approximation of Dulong and Petit announced in 1819 the heat capacity per gram atom is the same for all solid elements. Theoretical considerations by Boltzmann have shown that the law should refer to the

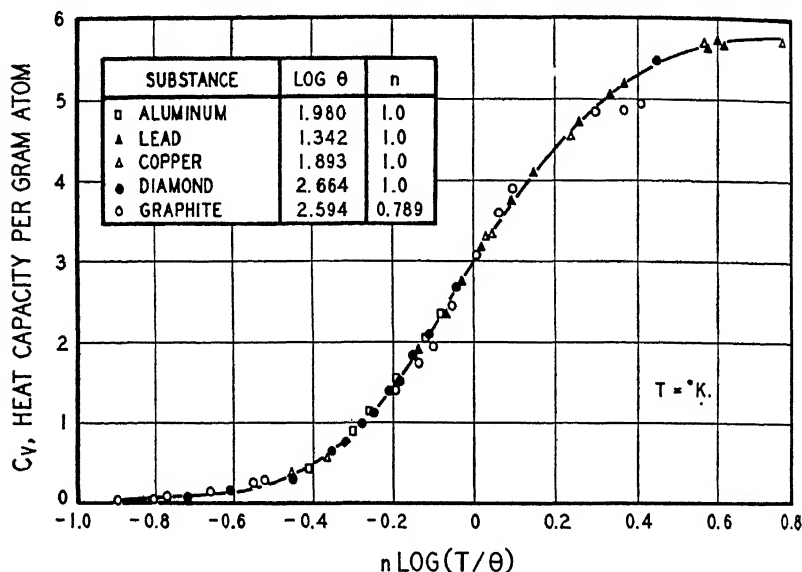


FIG. 1. Atomic Heat Capacity as a Function of Temperature.

heat capacity at constant volume and the constant should be 5.97 calories/(degree) (gram atom). Actually the value ordinarily used is 6.4, and, since for solids the difference between  $C_p$  and  $C_v$  is a small fraction of either, no distinction is usually made between the two. The rule fails for elements below potassium in atomic weight. It is approximately correct at room temperature or above. Indeed, the shape of the heat-capacity curve is found to be as indicated in Figure 1, and the atomic heat capacity of practically any solid element may be closely expressed by an equation of the type<sup>1</sup>

$$C_v = J \left( \frac{T}{\theta} \right)^n \quad (12)$$

where  $n$  is 1 for elements of simple crystalline form but has a smaller

<sup>1</sup> Lewis and Gibson, *J. Am. Chem. Soc.*, 39, 2554 (1917).

value for those of more complex structure,  $\theta$  is a constant characteristic of each element, and  $J$  is some function which is the same for all substances. For those substances where  $n = 1$  a single determination of  $C_v$  serves to fix the whole curve; for others, two values of  $C_v$  must be determined. A consideration of Figure 1 indicates why the Dulong and Petit approximation holds at room temperature or higher and fails at low temperatures.

If the heat-capacity curve for one element and two values on the curve of a similar element are available, by plotting as ordinates the temperature at which the first has certain values of heat capacity against the temperature at which the other has the same values, a straight line will

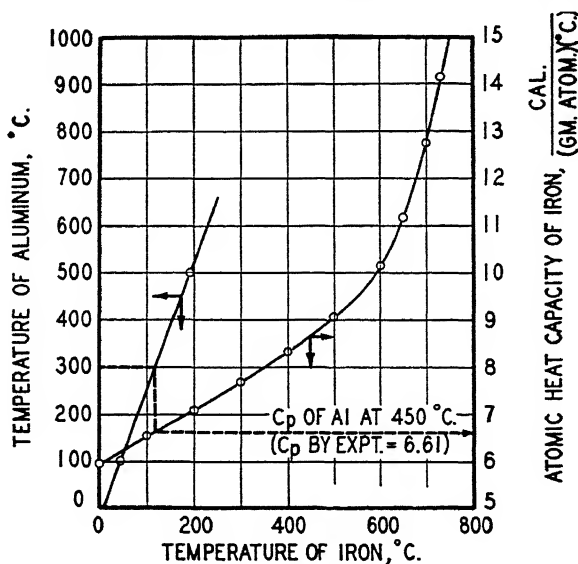


FIG. 2. Temperatures at which Iron and Aluminum have the same Atomic Heat Capacities. Based on data from Landolt-Börnstein, "Physikalische Tabellen," Vol. 3, pp. 2232-9.

be obtained. From this the heat capacity for the second element may be read at any temperature. Figure 2 shows such a plot for iron and aluminum.

**Kopp's Law for Solid Compounds.** It was natural to suppose that an approximation for solid compounds would be attempted in view of the value of the Dulong and Petit law. In 1864 Kopp announced the law bearing his name. He found the molal heat capacity at constant pressure and at 20°C. could be *approximated* by assuming it equal to the sum of the atomic heat capacities of the elements making up the

TABLE I  
CONSTANTS FOR KOPP'S LAW

Element	Heat Capacity
Heavy elements.....	6.4
Boron.....	2.7
Carbon.....	1.8
Fluorine.....	5.0
Hydrogen.....	2.3
Oxygen.....	4.0
Phosphorus.....	5.4
Silicon.....	3.5
Sulfur.....	5.4

compound. For Kopp's method the values given in Table I are recommended. Errors of 10 to 20 per cent are not uncommon when Kopp's approximation is used.

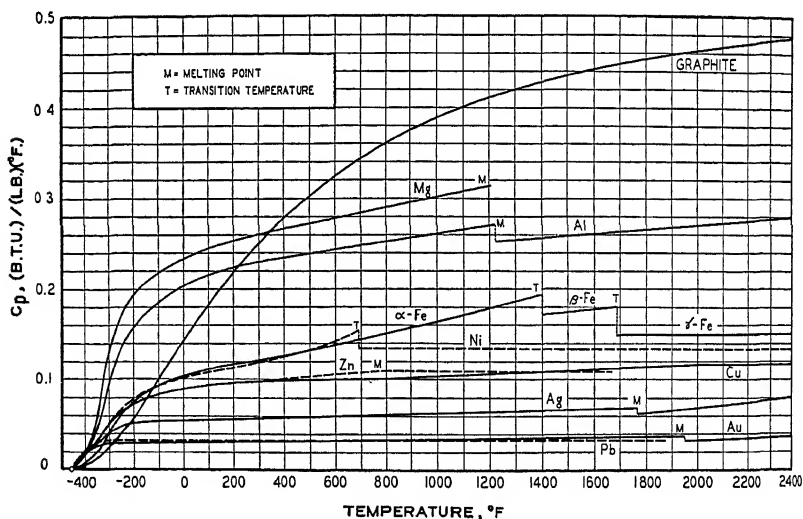


FIG. 3. Change in Heat Capacity of Some Elements with Temperature.

**Heat Capacity of Solids.<sup>1</sup>** Figures 3 and 4 give at various temperatures the instantaneous or true heat capacities for some industrially important solids.

<sup>1</sup> Kelley (U. S. Bureau of Mines, *Bulletin* 371) gives extensive data on the heat capacities of many solids and recommended equations expressing the results as a function of temperature. Figures 3 and 4 are based on data by Kelley.

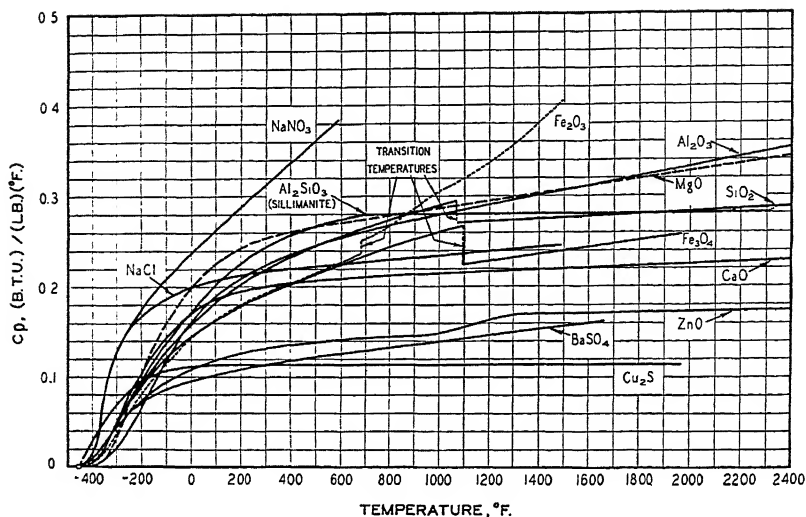


FIG. 4. Change in Heat Capacity of Compounds with Temperature.

**Heat Capacity of Pure Liquids and Solutions.** No useful approximations of general applicability are available for liquids. Although some tables of experimentally determined values are available, they are incomplete for most substances and entirely lacking for many.

For aqueous solutions of inorganic salts, the heat capacity may be estimated by assuming the dissolved salt to have a negligible heat capacity. Thus a 10 per cent by weight solution of NaCl in water would have an estimated heat capacity of 0.9, while a 30 per cent solution would have a heat capacity of 0.7. As might be expected, the rule is better for the more dilute solutions but is surprisingly good even for concentrations as great as 40 per cent.

**Heat Capacity of Gases.** The heat capacities of gases have been the subject of many investigations by experimenters and mathematicians. The results of these may be summed up briefly as follows:

1. For monatomic gases the value of  $Mc_v$  is about 3 and it does not change appreciably with temperature. For these gases the value of  $k$  is 1.67.
2. For diatomic gases the value of  $Mc_v$  is roughly 5 around 20°C., and at about this temperature change of  $Mc_v$  with temperature is usually small. For these gases the value of  $k$  is approximately 1.40–1.42.
3. For triatomic gases the value of  $Mc_v$  varies from 6 to 7 and changes rapidly with temperature. The value of  $k$  varies but is invariably smaller than that for the less complex molecules.

4. For gases having more than three atoms per molecule no generalizations are reliable. However, increasing molecular complexity is paralleled by increasing heat capacity, increased temperature coefficient of heat capacity, and decreasing value of  $k$ .

Owing to their industrial importance, empirical equations giving heat capacities as a function of temperature at atmospheric pressure have been developed for several common gases (Appendix II). Curves which

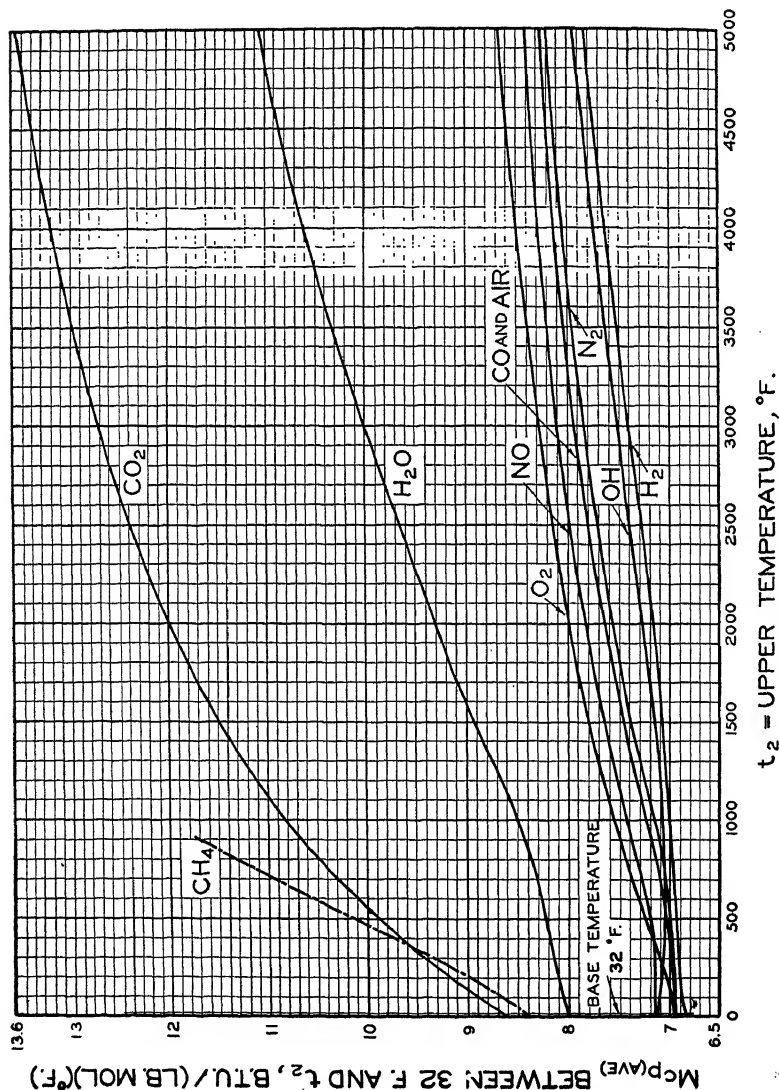


FIG. 5. Variation of  $(M_{CP})_{ave.}$  with Temperature for Gases.

are based on some of these are presented in Figure 5.<sup>1</sup> These give average  $Mc_p$  between 32°F. and any chosen upper temperature. These curves have been drawn for zero (extrapolated) pressure, but the values are practically the same at 1 atm.

As will be proved in a later chapter for the so-called perfect gases,

$$Mc_p - Mc_v = 1.987 \text{ cal./ (gm. mol) (}^{\circ}\text{C.) or B.t.u./ (lb. mol) (}^{\circ}\text{F.)}$$

This relation is often used for actual gases where data concerning the difference between  $Mc_p$  and  $Mc_v$  are lacking.

### HEAT OF REACTION

**Calorimetry.** The technique of measuring heat is called *calorimetry*, and the instrument in which the measurement is conducted, a *calorimeter*. Such measurements obviously imply the conservation of heat in its transfer from one body to another. The determination of heat quantities, by measuring the temperature change of a heat-absorbing medium of known heat capacity, constitutes one of the most important branches of experimental thermodynamics.

The bomb, the mixing, and the flow calorimeters are the most important types. In the *bomb* type, the change under investigation is conducted in a closed vessel of fixed volume strong enough to withstand any pressure developed. The heat of combustion of organic materials, including fuels, is frequently determined in this way. In the *mixing* calorimeter, the reacting materials are introduced and mixed, usually at ordinary pressure, and the heat evolved is measured. This type is employed for determining the heats of various chemical reactions usually between solids or between solids and liquids, when no gases or vapors are evolved. It is also the type often used for determining heat capacities of solids and liquids and heats of dilution. In the *flow* calorimeter

<sup>1</sup> Private communication from H. C. Hottel.

Sources of Data for Figure 5 are:

*Gas Authority and Reference*

- CH<sub>4</sub> Eucken and Lude, *Z. physik. Chem.*, **B5**, 436 (1929).
- CO Johnston and Davis, *J. Am. Chem. Soc.*, **56**, 271 (1934).
- CO<sub>2</sub> Kassel, *J. Am. Chem. Soc.*, **56**, 1838 (1934).
- H<sub>2</sub> Johnston and Davis, *J. Am. Chem. Soc.*, **56**, 1045 (1934).
- H<sub>2</sub>O Gordon, *J. Chem. Phys.*, **2**, 65, 549 (1934).
- N<sub>2</sub> Johnston and Davis, *J. Am. Chem. Soc.*, **56**, 271 (1934).
- NO Johnston and Chapman, *J. Am. Chem. Soc.*, **55**, 155 (1933).
- O<sub>2</sub> Lewis and von Elbe, *J. Am. Chem. Soc.*, **55**, 507 (1933).  
Lewis, private communication, 1935, to Hottel.
- OH Johnston and Dawson, *J. Am. Chem. Soc.*, **55**, 2744 (1933).



material being investigated is allowed to flow through the instrument, the change occurring and the heat quantities being measured under conditions of steady flow. This calorimeter is important for determining heat capacities of fluids, heats of condensation, and heats of combustion of fluid fuels.

In a bomb the operation is non-flow. Since the volume is constant, no expansion work is done on the surroundings. Furthermore, the nature of the instrument precludes the possibility of other work effects. By the first law equation,  $Q - W = \Delta E$ . The term  $W$  is zero, and the equation simplifies to  $Q = \Delta E$ . The bomb calorimeter is therefore a laboratory instrument for determining changes in internal energy. The constant-pressure mixing calorimeter is practically equivalent for those cases where volume changes during reaction are negligible, *e.g.*, reactions not involving evolution of gas.

In a flow calorimeter, operation is steady and the flow equation may be applied. As this instrument is used in the laboratory, differences in level between inlet and exit are negligible. Since it is customary to operate at low rates, kinetic-energy terms are inconsequential. In addition, the instrument performs no work effects on its surroundings other than those of intake and expulsion. For this case the flow equation simplifies to

$$Q = \Delta E + \Delta(PV) = \Delta H \quad (13)$$

A flow calorimeter as ordinarily employed is an instrument for direct, experimental determination of changes in enthalpy.

Experimental results from calorimeter measurements make possible calculation of  $\Delta E$  and  $\Delta H$  for the change the working substance has undergone. Because of the operation  $T_2$  seldom is equal to  $T_1$ , and yet it is desirable to report the  $\Delta E$  or  $\Delta H$  on an isothermal basis. Since in actual operation the temperature change is usually small, correction to an isothermal basis is readily and accurately accomplished.

Because the internal energy and enthalpy of a body depend on its condition or state, in reporting and using calorimetric results it is imperative that the initial and final states of all materials in question be given.

Internal energy and enthalpy are point functions, independent of path. For this reason the net change in  $E$  or  $H$  for several reactions occurring in series must be the sum of the individual changes. Thus, it is possible to oxidize ethyl alcohol to acetaldehyde, this in turn to acetic acid, and finally to carbon dioxide and water. It is not practical to determine the heat effects for these individual steps experimentally.

However, it is easy to oxidize completely any one of the three organic compounds by combustion in a bomb calorimeter, and thus determine the corresponding changes in internal energy.

For the individual oxidation steps the internal-energy changes are obviously the differences between the constant-volume heats of combustion for the corresponding compounds. This same principle makes possible determination of heat effects for reactions which will not of themselves go calorimetrically. Thus at room temperature hydrochloric acid gas may be decomposed into its elements only with difficulty and in no event under suitable calorimetric conditions. However, the union of hydrogen and chlorine to form hydrochloric acid gas goes easily and readily in a calorimeter. The change in internal energy or enthalpy is obviously numerically equal though opposite in sign to that of the reverse reaction.

**Heats of Reaction.** The heat effect occurring when a chemical reaction proceeds isothermally with no net useful work effects is called a **heat of reaction**. Two important cases are those at constant pressure and at constant volume. For the former, either non-flow or flow, the first law indicates

$$Q_{P,T} = \Delta H \quad (14)$$

For the latter, in the non-flow case,

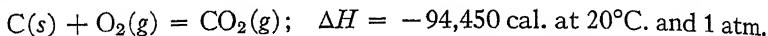
$$Q_{V,T} = \Delta E \quad (15)$$

The constant volume flow case for which  $Q_{V,T} = \Delta H_V$  is of little practical utility.

The bomb calorimeter measures the heat of reaction at constant volume; the flow calorimeter, if the inlet and outlet pressure be the same, measures the heat of reaction at constant pressure.

**Effect of Temperature at Constant Pressure (or Volume).** The experimental difficulty in operating a calorimeter at other than approximately room temperature is great. During the last decade the low-temperature calorimeter has been brought to a high state of development primarily for investigating heat capacities of substances at all temperatures to as near absolute zero as is experimentally possible. The difficulties here encountered were small compared with those to be surmounted in operating at high temperatures, yet data on heats of reaction at high temperatures are necessary in technical work. The heat of combustion of carbon with oxygen at 20°C. and 1 atm. is interesting, but since the burning of carbon-containing fuels is carried out commercially at much higher temperatures, it is at these temperature levels that the heat effect must be evaluated.

Both  $\Delta H$  and  $\Delta E$  are differences in point functions, and the same values for them must be obtained when passing from the same initial states to the same final states by different paths. For example,



This means that when 1 gram atom of solid carbon (as graphite) and 1 gram mol of oxygen gas each originally at  $20^\circ\text{C.}$  and 1 atm. react to form 1 gram mol of carbon dioxide gas at  $20^\circ\text{C.}$  and 1 atm., there are liberated 94,450 cal., *i.e.*, the enthalpy of the  $\text{CO}_2$  formed is 94,450 cal. less than the combined enthalpies of the carbon and oxygen, all measured above the same datum.

Note that the exact state of the system before and after the change must be definitely fixed. Often symbols are used to designate the solid, liquid, and gaseous states. Thus  $[\text{H}_2\text{O}]$  might signify the solid state;  $(\text{H}_2\text{O})$ , the gaseous; while  $\text{H}_2\text{O}$  would indicate the liquid. Similarly the three might be differentiated by  $\text{H}_2\text{O}(c)$ ,  $\text{H}_2\text{O}(g)$ , and  $\text{H}_2\text{O}(l)$ . When no statement is made to the contrary, it is assumed that each constituent is in that form in which it is stable at the temperature and pressure in question. Note also that a change which goes with heat evolution, a so-called exothermic change, corresponds to a decrease in  $H$  or  $E$ , whereas a change going with heat absorption, an endothermic change, corresponds to an increase in  $H$  or  $E$ .

This reversal of the sign of  $Q$  from that already decided is unfortunate. The thermochemist always calls  $Q_P$  or  $Q_V$  positive for decreases in  $H$  or  $E$ . It is better to express the heat effect as  $\Delta H$  or  $\Delta E$ , rather than  $Q$ .

To determine the enthalpy change for the reaction at  $500^\circ\text{C.}$  and 1 atm. from that at  $20^\circ$  and 1 atm. an enthalpy balance is used. Heat the carbon and oxygen separately at 1 atm. from  $20^\circ\text{C.}$  to  $500^\circ\text{C.}$  This constant-pressure heating results in changing the  $H$  of both constituents by an amount

$$\begin{aligned}\Delta H_1 \text{ for C} &= \int_{20^\circ}^{500^\circ} C_p dT \\ \Delta H_2 \text{ for O}_2 &= \int_{20^\circ}^{500^\circ} C_p dT\end{aligned}$$

Now allow the carbon and oxygen to react at  $500^\circ\text{C.}$  and 1 atm., giving  $\text{CO}_2$  at  $500^\circ\text{C.}$  and 1 atm. with a change in  $H$  of  $\Delta H_{500^\circ}$ .

The same final condition for  $\text{CO}_2$  (1 atm. and  $500^\circ\text{C.}$ ) could have been attained by reacting the C and  $\text{O}_2$  at  $20^\circ\text{C.}$  and 1 atm. with a change in  $H = \Delta H_{20^\circ}$ , and then heating the  $\text{CO}_2$  at 1 atm. from  $20^\circ\text{C.}$  to  $500^\circ\text{C.}$  for which

$$\Delta H_3 \text{ for CO}_2 = \int_{20^\circ}^{500^\circ} C_p dT$$

This would have resulted in bringing the system by a second path to its final state ( $\text{CO}_2$  at 1 atm. and  $500^\circ\text{C}.$ ).

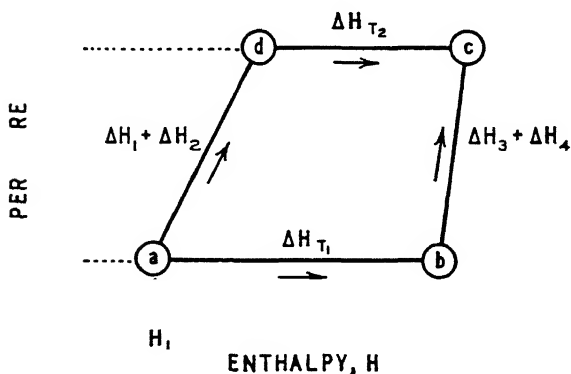
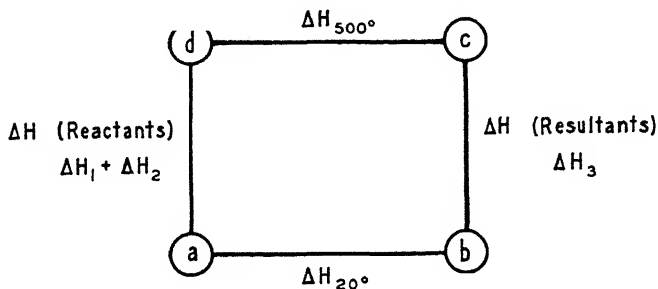
Expressed algebraically, the desired result is

$$+\Delta H_2 + \Delta H_{500^\circ} = +\Delta H_{20^\circ} + \Delta H_3 \quad (16)$$

In this particular example  $\Delta H_1$ ,  $\Delta H_2$ , and  $\Delta H_3$  are positive while  $\Delta H_{20^\circ}$  and  $\Delta H_{500^\circ}$  are negative. Or if the various values of  $C_p$  are assumed independent of temperature and no change in phase occurs,

$$C_p \Delta T_{\text{reactants}} + \Delta H_{500^\circ} = C_p \Delta T_{\text{resultants}} + \Delta H_{20^\circ} \quad (17)$$

$$= \Delta T(C_p \text{ resultants} - C_p \text{ reactants}) + \Delta H_{20^\circ} \quad (18)$$



FIGS. 6 and 7. Diagrams Illustrating Relation between Heats of Reaction at Different Temperatures.

It is customary to illustrate this procedure diagrammatically as indicated on Figure 6. The change in enthalpy from  $a$  to  $c$  along  $abc$  must be equal to the enthalpy change from  $a$  to  $c$  along  $adc$ . Instead of by Figure 6, the calculation for change in heat of reaction with temperature

may be graphically indicated by a temperature-enthalpy diagram (Figure 7). In both figures the points correspond.

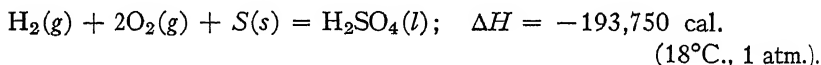
Equations analogous to those previously derived may be formulated for the change in heat of reaction with temperature at constant volume. For the constant-pressure change an enthalpy balance was used; for the constant-volume, an internal energy balance should be employed.

**Effect of Pressure (or Volume) at Constant Temperature.** To calculate the effect of pressure on heat of reaction, either an internal energy or enthalpy balance should be used. In general

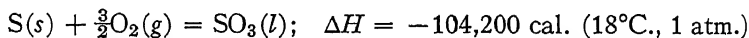
$$\begin{aligned} \Delta H_{T_1, P_1} + \int_{P_1}^{P_2} \left( \frac{\partial H}{\partial P} \right)_T dP_{(\text{resultants})} \\ = \Delta H_{T_1, P_2} + \int_{P_1}^{P_2} \left( \frac{\partial H}{\partial P} \right)_T dP_{(\text{reactants})} \end{aligned} \quad (19)$$

Similar expressions can be derived for the change in  $\Delta E$  with respect to volume at constant  $T$ . For most cases corrections due to pressure may be neglected, but this is not true in many modern high-pressure processes.

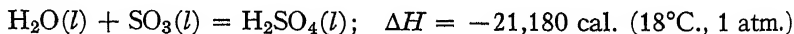
**Thermal Data.** To record the thermal data for every possible chemical reaction and change for which values of  $\Delta H$  or  $\Delta E$  are desired would be time consuming and laborious. Fortunately, this is not necessary. Since  $E$  and  $H$  are point functions, changes in these for any chemical reaction may be calculated *by algebraically* adding individual values for a series of reactions, the net effect of which is equivalent to that desired. For example,<sup>1</sup>



But also



Therefore,



A simple procedure is to record the changes for reactions which yield the various compounds from the elements. Such values of  $\Delta H$  and  $\Delta E$  are known as heats of formation. (See Table II.)

<sup>1</sup> Heats of reaction are from Bichowsky and Rossini, "Thermochemistry of Chemical Substances," New York, Reinhold Publishing Corp., 1936.

TABLE II — HEATS OF FORMATION AT 18°C. AND 1 ATM.\*

 $Q = -\Delta H$  in kilogram calories per gram formula weight.

AgCl	(c)	30.7	HCHO	(g)	28.7
AgNO <sub>3</sub>	(c)	29.4	H <sub>2</sub> CO <sub>3</sub>	(dil.)	167.58
Al(OH) <sub>3</sub>	(c)	304.9	HCN	(g)	-30.7
Al <sub>2</sub> O <sub>3</sub>	(c)	380.0	KOH	(c)	102.02
B <sub>2</sub> O <sub>3</sub>	(glass)	279.9	KCl	(c)	104.361
BaCl <sub>2</sub>	(c)	205.28	K <sub>2</sub> SO <sub>4</sub>	(c)	342.66
BaSO <sub>4</sub>	(c)	349.4	K <sub>2</sub> CO <sub>3</sub>	(c)	274.46
CO	(g)	26.84	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	(c)	488.5
CO <sub>2</sub>	(g)	94.45	K <sub>2</sub> CrO <sub>4</sub>	(c)	333.4
CH <sub>4</sub>	(g)	18.24	KSCN	(c)	47.40
C <sub>2</sub> H <sub>2</sub>	(g)	-53.9	KCN	(c)	28.5
C <sub>2</sub> H <sub>4</sub>	(g)	-11.0	KBr	(c)	94.07
C <sub>2</sub> H <sub>6</sub>	(g)	20.96	KI	(c)	78.87
CH <sub>3</sub> OH	(l)	57.45	MnO <sub>2</sub>	(c)	123.0
CH <sub>3</sub> COONH <sub>4</sub>	(c)	149.0	MgCO <sub>3</sub>	(c)	268
(COOH) <sub>2</sub>	(c)	197.6	NO	(g)	-21.6
C <sub>2</sub> H <sub>5</sub> OH	(l)	67.14	NO <sub>2</sub>	(g)	-8.03
(CH <sub>3</sub> OH) <sub>2</sub>	(l)	112.1	N <sub>2</sub> O	(g)	-19.65
CCl <sub>4</sub>	(l)	33.8	N <sub>2</sub> O <sub>3</sub>	(g)	-20.0
CS <sub>2</sub>	(l)	-15.4	N <sub>2</sub> O <sub>4</sub>	(g)	-3.06
C <sub>2</sub> N <sub>2</sub>	(g)	-71	N <sub>2</sub> O <sub>5</sub>	(g)	-0.6
Cd(Cl) <sub>2</sub>	(c)	93.0	NH <sub>3</sub>	(g)	11.0
CdSO <sub>4</sub>	(c)	222.22	NH <sub>4</sub> NO <sub>3</sub>	(c)	87.13
CdS	(c)	34.6	NH <sub>4</sub> Cl	(c)	74.95
Cd(NO <sub>3</sub> ) <sub>2</sub>	(c)	77	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	(c)	281.46
CaO	(c)	38.5	NH <sub>4</sub> HCO <sub>3</sub>	(c)	203.0
CuCl <sub>2</sub>	(c)	53.4	(NH <sub>2</sub> ) <sub>2</sub> CO	(c)	78.5
Cu <sub>2</sub> Cl <sub>2</sub>	(c)	68.6	NaOH	(c)	101.96
CuSO <sub>4</sub>	(c)	184.7	NaCl	(c)	98.330
Cu(NO <sub>3</sub> ) <sub>2</sub>	(c)	73.1	Na <sub>2</sub> S	(c)	89.8
CaO	(c)	151.7	Na <sub>2</sub> SO <sub>3</sub>	(c)	261.2
Ca(OH) <sub>2</sub>	(c)	236.0	Na <sub>2</sub> SO <sub>4</sub>	(c)	330.48
CaCl <sub>2</sub>	(c)	190.6	NaHSO <sub>4</sub>	(c)	269.04
CaSO <sub>4</sub>	(c)	340.4	NaNO <sub>3</sub>	(c)	111.72
CaCO <sub>3</sub>	(c)	289.5	Na <sub>2</sub> CO <sub>3</sub>	(c)	269.89
FeO	(c)	64.3	Na <sub>2</sub> C <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	(c)	171.34
Fe <sub>2</sub> O <sub>3</sub>	(c)	198.5	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	(c)	742.6
Fe <sub>3</sub> O <sub>4</sub>	(c)	266.9	Na <sub>2</sub> CrO <sub>4</sub>	(c)	319.8
FeCl <sub>3</sub>	(c)	96.4	P <sub>2</sub> O <sub>5</sub>	(c)	360.0
FeS <sub>2</sub>	(c)	35.5	PbO <sub>2</sub>	(c)	65.0
H <sub>2</sub> O	(l)	68.370	PbO	(c)	52.46
H <sub>2</sub> O <sub>2</sub>	(l)	45.20	Pb <sub>2</sub> O <sub>4</sub>	(c)	172.4
HF	(g)	64.0	PbSO <sub>4</sub>	(c)	218.5
HCl	(g)	22.06	Pb(NO <sub>3</sub> ) <sub>2</sub>	(c)	106.89
HBr	(g)	8.65	SO <sub>2</sub>	(g)	70.92
HI	(g)	-5.91	SO <sub>3</sub>	(g)	93.9
H <sub>2</sub> S	(g)	5.3	SiO <sub>2</sub>	(lass)	201.0
H <sub>2</sub> SO <sub>4</sub>	(l)	193.75	Zn(OH) <sub>2</sub>	(c)	155.8
HNO <sub>3</sub>	(g)	34.4	Zn(Cl) <sub>2</sub>	(c)	99.55
H <sub>3</sub> PO <sub>3</sub>	(c)	228.93	ZnS	(c)	44
H <sub>3</sub> PO <sub>4</sub>	(c)	303.37	ZnSO <sub>4</sub>	(c)	233.4
HCOOH	(g)	88.65	ZnO	(c)	83.5

In above table: dil. = dilute aqueous solution; g = gas; c = crystalline; l = liquid.

\* Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing

To obtain the values in Table II, all the elements in their usual stable state at 18°C. and 1 atm. are arbitrarily assigned the same relative value of  $H$  or  $E$ , usually zero *for purposes of these calculations*. This does not mean that absolute  $H$  or  $E$  for the element is zero at 18°C. and 1 atm. for other calculations. For elements which exist in several different forms at 18°C. and 1 atm., confusion may arise unless the form for which  $H$  or  $E$  is assumed zero is specified. Thus carbon can exist in several forms at 18°C. and 1 atm., *i.e.*, amorphous, graphite, and diamond. Usually graphitic carbon or the diamond form is assigned a value of  $H = 0$ .

It is preferable to select all thermal data for any desired calculation from the recorded results of a single reliable experimenter. Probably many of his recorded results are obtained by subtraction of two large values. These, if used with data from a second equally reliable experimenter, might introduce a large error. This difficulty is obviated by selecting all data from the same investigator.

**Heats of Solution and Dilution.** These are best classed as heats of reaction, and results may be calculated as indicated in the previous pages.

### SUMMARY

In this chapter the various heat capacities were defined and certain general thermodynamic relations between them were pointed out.

Approximate methods of estimating heat capacities such as the laws of Dulong and Petit and of Kopp were given.

A heat of reaction at constant volume is a change in internal energy; the similar effect at constant pressure is a change in enthalpy.

Depending on the fact that internal energy and enthalpy are point functions, methods of calculating heats of reaction at one temperature from those at another were developed. A similar calculation for the effect of pressure (or volume) was presented.

### NOTATION FOR CHAPTER V

#### *Upper Case:*

- $C$  Atomic or molal heat capacity ( $= Mc$ )
- $E$  Internal energy
- $H$  Enthalpy ( $E + PV$ )
- $J$  Function in Equation 12
- $M$  Molecular weight
- $P$  Absolute pressure
- $Q$  Heat interchanged with surroundings
- $T$  Absolute temperature
- $V$  Volume
- $W$  Work done by system

*Lower Case:*

- $c$  Specific heat capacity (per unit mass)
- ( $c$ ) Crystalline state
- $d$  Differential
- ( $g$ ) Gaseous state
- $k$  Ratio of  $C_p$  to  $C_v$ ; or ratio of  $Mc_p$  to  $Mc_v$
- ( $l$ ) Liquid state
- $n$  Constant in Equation 12
- ( $s$ ) Solid state
- $t$  Temperature

*Greek Letters:*

- $\partial$  Partial differential
- $\Delta$  Final value — Initial value
- $\theta$  Constant, characteristic of an element in Equation 12

*Subscripts:*

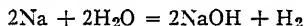
- $P, p$  Constant pressure
- $T, t$  Constant temperature
- $V, v$  Constant volume

## PROBLEMS

1. The heat of combustion at 20°C. and 1 atm. for decane is 1613.8 k. cal./gm. mol; for pentane, 834.6 k. cal./gm. mol; and for pentene, 804.4 k. cal./gm. mol. Estimate the heat of cracking of decane assuming that it goes to pentane and pentene.

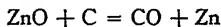
2. The heating value of a certain oil as determined in a bomb calorimeter is 17,670 B.t.u./lb. at 20°C. The composition of the oil may be accurately expressed by the formula  $(CH_2)_n$ . If this oil is completely burned under a boiler with 25 per cent excess air, the flue gases leaving the boiler at 500°F. and 1 atm., how many B.t.u. are available for absorption by the boiler per pound of fuel burned?

3. It is proposed to make solid NaOH by reacting metallic Na at 68°F. with dry saturated steam at 150 lb./sq. in. abs., the solid NaOH and the hydrogen formed being removed from the reactor at 358.4°F.



Per 100 lb. of NaOH formed, how many B.t.u. must be added to or withdrawn from the reactor? Molal specific heat of NaOH is approximately 12.5.

4. In one method of producing metallic zinc, the oxide mixed with powdered coke is heated in clay retorts, the metallic zinc being distilled as a vapor from the retorts. The reaction is essentially



Per 100 lb. of zinc produced, how many B.t.u. must be transmitted through the walls of the retort? Assume the ZnO and coke to enter at 20°C.

5. When  $H_2SO_4$  is diluted with water, according to Thomsen ("Thermochemistry," p. 75, London, Longmans, Green & Co., 1908), the heat evolved may be closely



approximated by the formula

$$\frac{n(17,860)}{n + 1.7983} \text{ cal. at } 18^{\circ}\text{C. and 1 atm. for values of } n \text{ not over 20}$$

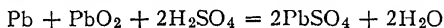
where  $n$  = mols of water per mol of  $\text{H}_2\text{SO}_4$ .

In a plant making 90 per cent acid by burning sulfur, how many B.t.u. must be lost per ton of 90 per cent acid produced?

6. Eighty per cent  $\text{H}_2\text{SO}_4$  is to be made by mixing 50 per cent  $\text{H}_2\text{SO}_4$  and 93 per cent  $\text{H}_2\text{SO}_4$  in a suitably jacketed mixing kettle.

If the 93 per cent acid enters the mixer at  $180^{\circ}\text{F.}$ , the 50 per cent acid at  $60^{\circ}\text{F.}$ , and the 80 per cent mixture leaves at  $110^{\circ}\text{F.}$ , how many B.t.u. must be lost from the mixing kettle per ton of 80 per cent acid produced? For the purposes of this problem, the heat capacity of sulfuric acid solutions may be assumed 2.3 joules per gram of solution per degree Centigrade.

7. Assume that in a lead storage cell the reaction is



A series of 16 such cells is operating a 32-volt  $\frac{1}{2}$ -hp. motor having an efficiency of 90 per cent. Estimate, per horsepower-hour of work performed by the motor, the heat evolved by the battery, assuming the temperature of the latter constant at  $18^{\circ}\text{C.}$

8. A mixture of equimolal quantities of  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$  is to be heated from 60 to  $200^{\circ}\text{F.}$  Estimate, per ton of mixture, the amount of heat required.

9. The heat of combustion of a light liquid hydrocarbon determined in a bomb calorimeter at  $20^{\circ}\text{C.}$  is 18,000 B.t.u./lb. The composition of the hydrocarbon may be represented by the formula  $(\text{CH}_2)_n$ . If this could be completely burned in an internal-combustion engine with 100 per cent excess air, the air-fuel mixture entering at  $20^{\circ}\text{C.}$  and 1 atm., the exhaust gases leaving at  $400^{\circ}\text{C.}$  and 1 atm., the engine developing 1.4 hp-hr. of work per pound of fuel burned, estimate how much heat would have to be removed by the cooling jackets per pound of fuel burned.

10. If the above-mentioned fuel were burned at atmospheric pressure with 25 per cent excess air (air at  $20^{\circ}\text{C.}$ ) to supply heat for a chemical process being carried out at  $1000^{\circ}\text{C.}$ , how many B.t.u. per pound of fuel burned would be available for the reaction?

## CHAPTER VI

### PROPERTIES OF MATERIALS

Although thermodynamics deals with the energy transformations accompanying changes in the conditions under which matter exists, before these can be expressed quantitatively in any generalized way, comprehensive data on the properties of materials must be available. This chapter will be devoted to presenting some of the available information on the properties of substances. Such a presentation is peculiarly difficult for the chemical engineer because of the variety of systems with which he must deal.

The properties of any system must ultimately be determined by experiment. To facilitate analysis on the behavior of a system under varying conditions, it is desirable to have its properties systematically organized and arranged. This is done in a number of ways:

1. By diagrams.
2. By tables.
3. By algebraic equations.

Sometimes it is possible to formulate an approximate generalized relationship applicable to whole groups of substances and involving the use of one or more of the preceding methods of presentation. Such a method, considered in detail in the latter part of this chapter, is especially valuable where the available data are limited.

**Diagrams.** Diagrams of the type under discussion are employed for two purposes: (1) to present graphically the interrelations of physical properties when these can be represented as point functions; (2) to represent, by plotting changes in physical properties, the path followed when a system undergoes a definite change.

In monovariant changes of state, since the intensive properties are functions of a single independent variable, all may be plotted against any one arbitrarily chosen as the independent variable. Temperature is almost always chosen for the independent variable. Thus, the pressure exerted by a given monovariant system may be plotted against the temperature, the so-called vapor pressure curve (Figure 1); the specific volumes or the densities of the individual phases may be similarly plotted (Figures 2 and 3); the specific internal energy, the specific enthalpy, or any intensive property may be treated in like manner.

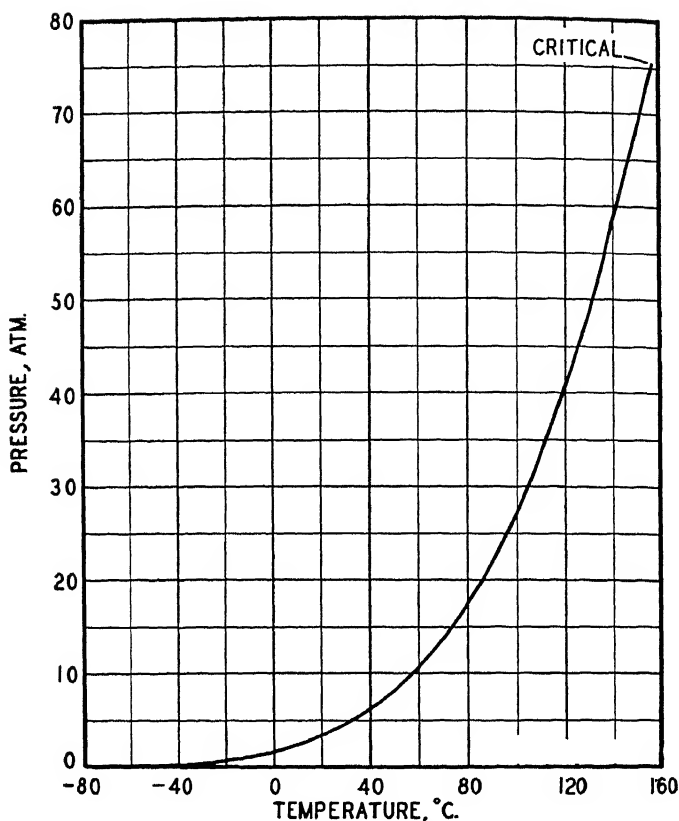


FIG. 1. Vapor-Pressure Curve for Sulfur Dioxide. Based on data from the "International Critical Tables," Vol. 3, p. 236.

The treatment of divariant systems, involving two independent variables, requires the equivalent of a three-dimensional diagram; this is almost always represented by plotting, on a plane diagram, curves along which some intensive variables (other than those represented on the axes) are held constant. Thus, on Figure 4, lines of constant temperature, isotherms, are plotted on a  $P$ - $H$  plane.

**Phase Diagrams.** Another common type of diagram previously discussed in Chapter IV is the phase diagram. Usually this is a plot of pressure versus temperature, showing for various phases the relations as required by the phase rule. Especially as applied to single-component systems, these diagrams are closely related to thermodynamic diagrams mentioned in this chapter. It is instructive to compare phase diagrams with some of the common thermodynamic diagrams such as

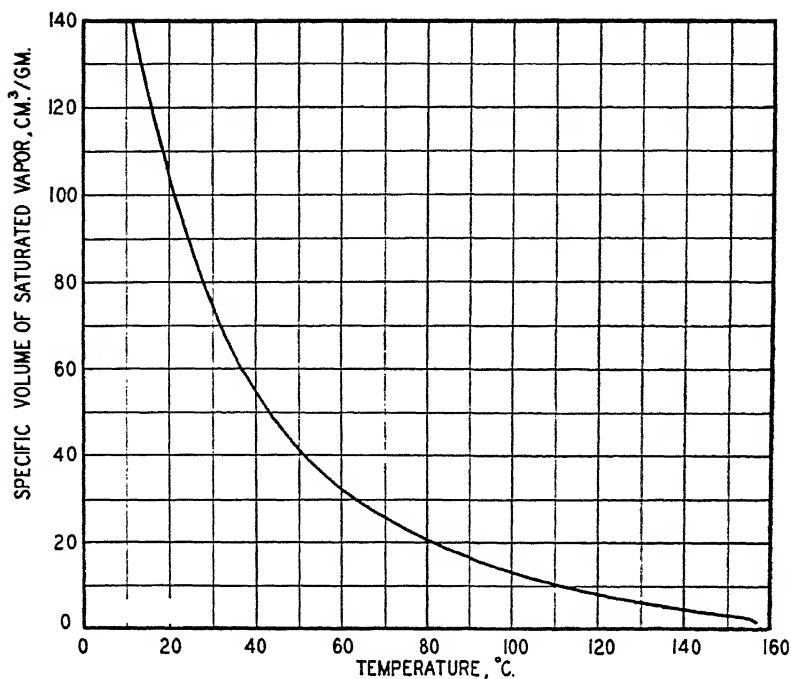


FIG. 2. Specific Volume of Saturated Sulfur Dioxide Vapor. Based on data from the "International Critical Tables," Vol. 3, p. 236.

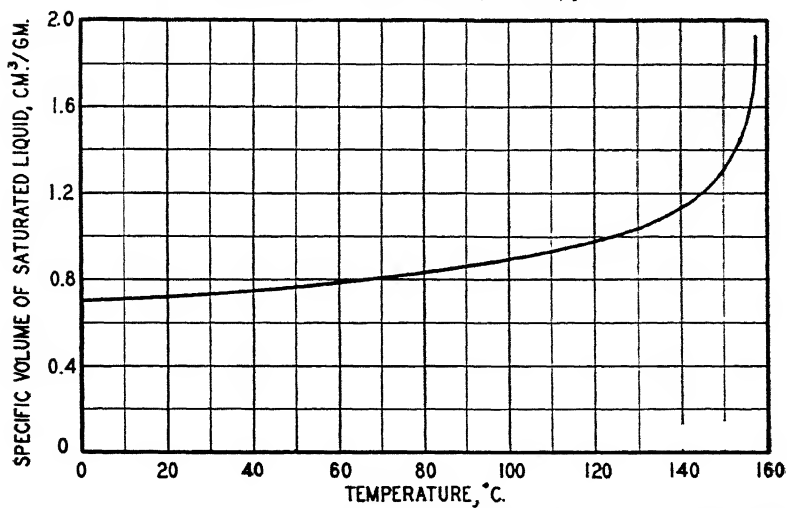


FIG. 3. Specific Volume of Saturated Sulfur Dioxide Liquid. Based on data from the "International Critical Tables," Vol. 3, p. 236.

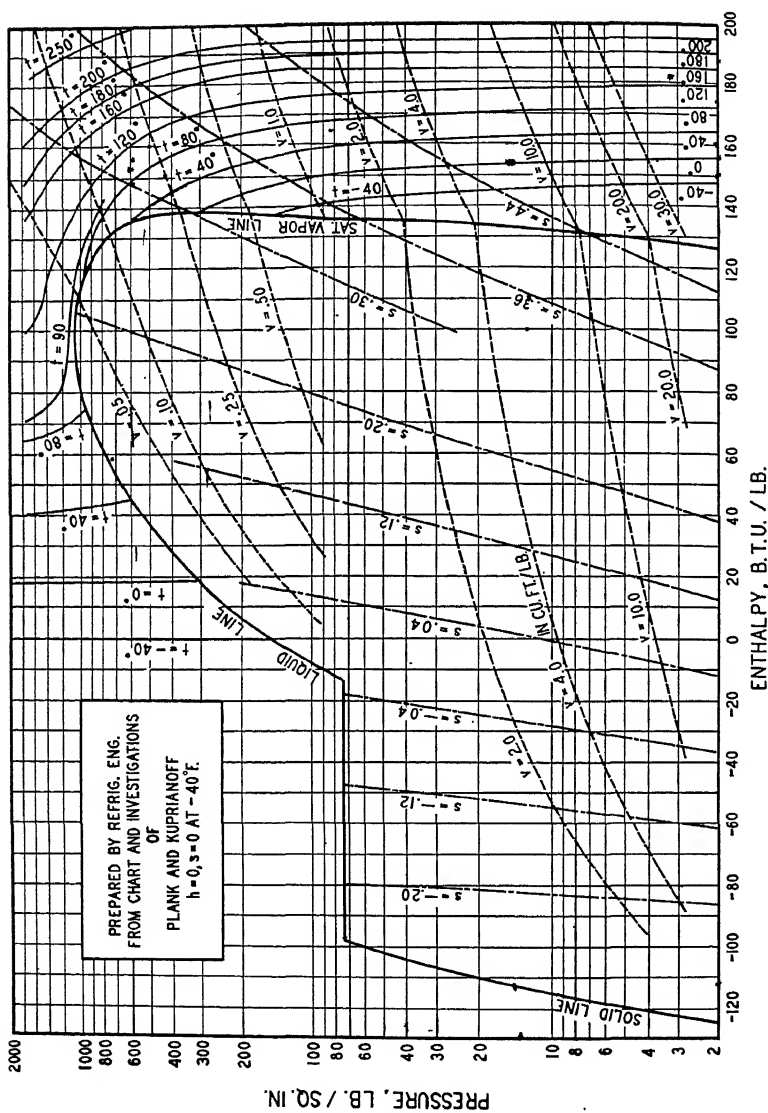


Fig. 4. Pressure-Enthalpy Diagram for Carbon Dioxide.

the pressure-enthalpy diagram for  $\text{CO}_2$ , Figure 4. This figure gives all the information contained on the phase diagram and, in addition, the distribution of matter between the various phases, a point on which the phase rule offers no information. On the thermodynamic diagram, triple points become lines and phase boundary lines become areas. Very often construction of the more simple phase diagram will be found helpful as a preliminary step in drawing thermodynamic diagrams.

**Tables.** In complicated cases the tabular form is a convenient method for presenting data. Single-component, one-phase systems, such as *superheated vapors* or gases, are important examples. In these cases there are two independent variables, and double columns are required to present tabulated values, as for example in Keenan and Keyes' superheated steam tables (Table I). Referring to the last four vertical

TABLE I  
PROPERTIES OF SUPERHEATED STEAM  
(Keenan and Keyes, "Thermodynamic Properties of Steam,"  
John Wiley & Sons, New York, 1936)

Abs. Pres. lb. in. <sup>2</sup> (Sat. Temp.)		Saturated		Superheated Vapor — degrees Fahrenheit			
		Liquid	Vapor	200°	400°	600°	800°
1 (101.74)	<i>v</i>	0.02	333.6	392.6	512.0	631.2	750.4
	<i>h</i>	69.7	1106.0	1150.4	1241.7	1335.7	1432.8
	<i>s</i>	0.1326	1.9782	2.0512	2.1720	2.2702	2.3542
14.696 (212.00)	<i>v</i>	0.02	26.80	.....	34.68	42.86	51.00
	<i>h</i>	180.1	1150.4	.....	1239.9	1334.8	1432.2
	<i>s</i>	0.3120	1.7566	.....	1.8743	1.9734	2.0576
100 (327.81)	<i>v</i>	0.018	4.432	.....	4.937	6.218	7.446
	<i>h</i>	298.4	1187.2	.....	1227.6	1329.1	1428.9
	<i>s</i>	0.4740	1.6026	.....	1.6518	1.7581	1.8443
500 (467.01)	<i>v</i>	0.0197	0.9278	.....	.....	1.1591	1.4405
	<i>h</i>	449.4	1204.4	.....	.....	1298.6	1412.1
	<i>s</i>	0.6487	1.4634	.....	.....	1.5588	1.6571

columns, it is readily seen that the values given in each are at a fixed temperature. As read horizontally the values are at constant pressures but variable temperature. At each intersection, the tables give for 1 lb. of steam three intensive properties: specific volume, *v*; specific enthalpy, *h*; and specific entropy, *s*.<sup>1</sup> In the extreme left column, the

<sup>1</sup> The entropy is a property which will be studied in detail later.

saturation temperature is given in parentheses below the corresponding pressure. It will be remembered that this temperature is that below which, under stable conditions, steam cannot exist as vapor at the pressure in question. Conditions intermediate between these appearing in the table itself must be obtained by interpolation (sometimes by double interpolation), but error due to this is rendered negligible by the multiplicity of points recorded.

Table II, giving the properties of saturated steam, refers to a single-component homogeneous system. There is but one independent variable. One may arbitrarily, within certain limits, state the pressure, the temperature, or any other single intensive variable. Fixing one will fix all. From a consideration of the phase rule the beginner might treat this as a divariant system, but it is specifically stated that the steam must always remain saturated. This in itself places one limitation on the system, *i.e.*, fixes one independent variable.

TABLE II  
PROPERTIES OF SATURATED STEAM\*  
(Keenan and Keyes, "Thermodynamic Properties of Steam,"  
John Wiley & Sons, New York, 1936.)

Pres.	Temp.	Specific Volume		Enthalpy			Entropy			Internal Energy		
lb/in. <sup>2</sup>		cu. ft./lb.		B.t.u./lb.			B.t.u./(lb.) (°F.)			B.t.u./lb.		
<i>P</i>	<i>t</i>	<i>v<sub>f</sub></i>	<i>v<sub>g</sub></i>	<i>h<sub>f</sub></i>	<i>h<sub>fg</sub></i>	<i>h<sub>g</sub></i>	<i>s<sub>f</sub></i>	<i>s<sub>fg</sub></i>	<i>s<sub>g</sub></i>	<i>e<sub>f</sub></i>	<i>e<sub>fg</sub></i>	<i>e<sub>g</sub></i>
0.20	53.14	0.01603	1526.0	21.21	1063.8	1085.0	0.0422	2.0741	2.1163	21.21	1007.3	1028.5
14.70	212.00	.01672	26.80	180.07	970.3	1150.4	3120	1.4446	1.7566	180.02	897.5	1077.5
100	327.81	.01774	4.432	298.40	888.8	1187.2	4740	1.1286	1.6026	298.08	807.1	1105.2
200	381.79	.01839	2.288	355.36	843.0	1198.4	5435	1.0018	1.5453	354.68	759.0	1113.7
500	467.01	.0197	.9278	449.4	755.0	1204.4	6487	0.8147	1.4634	447.6	671.0	1118.6

\* In tables of this type, based on one pound of substance and compiled primarily for engineering work, it is common practice to use small letters, *e*, *h*, *v*, *s*, etc., as symbols for the various properties recorded, as has been done in the first five tables of this chapter. Throughout the rest of this book, however, capital letters are used generally whether the amount of material under discussion is unity or not.

Any table must be based on a definite quantity of material. Usually in engineering work this is the pound; in scientific work, the gram. In addition, values of such quantities as internal energy, enthalpy, and entropy are recorded above some arbitrarily chosen zero datum. In Keenan and Keyes' tables, values of enthalpy are recorded above that for liquid water at 32°F. and under its own vapor pressure. It is interesting for the student to show that at this condition the numerical

TABLE III

## PROPERTIES OF SATURATED SULFUR DIOXIDE

("The Refrigerating Data Book," Am. Soc. Refrig. Eng., 1939-1940, p. 128.)

Temp.	Pres. (Abs.)	Vapor Vol.	Liquid Dens.	Enthalpy (above $-40^{\circ}\text{F.}$ )			Entropy (above $-40^{\circ}\text{F.}$ )	
$^{\circ}\text{F.}$	lb., in. <sup>2</sup>	ft. <sup>3</sup> , lb.	lb./ft. <sup>3</sup>	B.t.u., lb.			B.t.u./ (lb.) ( $^{\circ}\text{F.}$ )	
$t$	$P$	$v_g$	$\rho_f$	$h_f$	$h_{fg}$	$h_g$	$s_f$	$s_g$
-40	3.136	22.42	95.79	0.00	178.61	178.61	0.00000	0.42562
0	10.35	7.280	92.42	12.44	170.63	183.07	.02795	.39917
+40	27.10	2.887	88.81	26.12	159.25	185.37	.05668	.37541
80	59.68	1.321	85.03	40.05	145.12	185.17	.08399	.35296
120	120.93	0.660	80.90	53.58	128.78	182.36	.10829	.33046

value of the internal energy must be negative. In like manner the entropy for liquid water at these conditions is chosen as zero. Not all tables use the same datum. Thus, for some refrigerating fluids in the United States, the enthalpy of the liquid at its saturation pressure at  $-40^{\circ}\text{F.}$  is chosen as zero (Table III). In Table IV, the datum for enthalpy is  $-148.0^{\circ}\text{F.}$ ; in Table V,  $0.0^{\circ}\text{F.}$

TABLE IV

## PROPERTIES OF SATURATED ETHANE

("The Refrigerating Data Book," Am. Soc. Refrig. Eng., 1934, p. 36.)

Temp.	Abs. Pres.	Vapor Vol.	Liquid Dens.	Enthalpy (above $-148^{\circ}$ )		Entropy (above $-148^{\circ}$ )	
$^{\circ}\text{F.}$	lb./in. <sup>2</sup>	ft. <sup>3</sup> , lb.	lb./ft. <sup>3</sup>	B.t.u., lb.		B.t.u., lb.	
$t$	$P$	$v_g$	$\rho_f$	$h_f$	$h_g$	$s_f$	$s_g$
-148.0	7.62	14.1	35.00	0.0	219.1	0.000	0.703
-58.0	80.28	1.60	30.76	54.2	238.2	0.151	0.609
-0.4	217.6	0.582	27.33	98.0	252.4	0.250	0.587
+32.0	345.7	0.346	24.95	128.2	258.7	0.312	0.577
+86.0	675.9	0.118	17.20	195.0	244.0	0.439	0.529

Table VI indicates one method of presenting  $P$ - $V$ - $T$  relations. Here the  $PV$  product has arbitrarily been chosen equal to unity at  $0^{\circ}\text{C.}$  and



TABLE V

## PROPERTIES OF SATURATED ISOBUTANE

("The Refrigerating Data Book," Am. Soc. Refrig. Eng., 1934, p. 38.)

Temp.	Abs. Pres.	Vapor Vol.	Liquid Dens.	Enthalpy (above 0°F.)		Entropy (above 0°F.)	
°F.	lb./in. <sup>2</sup>	ft. <sup>3</sup> /lb.	lb./ft. <sup>3</sup>	B.t.u./lb.		B.t.u./lb.	
<i>t</i>	<i>P</i>	<i>v<sub>g</sub></i>	<i>ρ<sub>f</sub></i>	<i>h<sub>f</sub></i>	<i>h<sub>g</sub></i>	<i>s<sub>f</sub></i>	<i>s<sub>g</sub></i>
-20.0	7.50	11.0	38.35	-9.0	156.5	-0.020	0.356
0	11.6	7.17	37.60	0.0	160.5	0.000	0.350
25	20.2	4.24	36.60	13.0	167.5	0.027	0.346
50	32.5	2.71	35.60	27.0	175.5	0.055	0.346
75	49.7	1.79	34.60	43.0	185.0	0.086	0.351
100	73.7	1.23	33.45	61.0	195.5	0.118	0.359

1 atm., and all other values are given relative to this datum.<sup>1</sup> To evaluate the actual volume at any pressure and temperature requires, in addition to this table, information on either the density or the specific volume at 0°C. and 1 atm.; e.g., density of CO<sub>2</sub> at 0°C., 1 atm., is 1.9769 gm./liter.<sup>2</sup>

TABLE VI

*P-V-T* RELATIONS FOR CARBON DIOXIDE

("International Critical Tables," Vol. 3, p. 11.)

<i>P</i> , atm.	Values of <i>PV</i>				
	0°C.	20°C.	40°C.	60°C.	80°C.
1	1.0000	.....	.....	.....	.....
100	0.2020	0.2285	0.3090	0.6610	0.8725
200	0.3850	0.4190	0.4675	0.5425	0.6600
300	0.5595	0.5985	0.6485	0.7100	0.7900
400	0.7280	0.7710	0.8230	0.8840	0.9560
500	0.8905	0.9380	0.9900	1.0540	1.1240

<sup>1</sup> Dividing any recorded value of *PV* in Table VI by the corresponding pressure gives the numerical value of the volume in Amagat units. The Amagat density is the reciprocal of the Amagat volume.

<sup>2</sup> "International Critical Tables," Vol. 3, p. 3.

When dealing with mixtures of saturated vapors and small quantities of their saturated liquids, it is usual to refer to that fraction of the total quantity present as vapor as the quality. A mixture 5 per cent by weight liquid water and 95 per cent by weight water vapor in equilibrium would be referred to as steam of 0.95 quality or 95 per cent.

### ALGEBRAIC PRESENTATION OF DATA

Many algebraic expressions have been proposed to represent the experimental pressure-volume-temperature data on gases. Such an equation in terms of these three variables is an *equation of state*. To determine all thermodynamic properties of a substance requires, in addition to an equation of state, some data on the thermal characteristics, usually heat capacities.

Of the many proposed equations of state, practically all of which have some theoretical basis, those of van der Waals, Dieterici, Berthelot, Keyes, and Beattie and Bridgeman may be mentioned. All these suffer either because of limited applicability or difficulty in mathematical manipulation.

The equation of Beattie and Bridgeman probably offers the closest check with the experimental data as applied to widely differing substances and over considerable ranges. However, this equation like most others is not reliable above the critical density. The Beattie-Bridgeman equation<sup>1</sup> is

$$P = \frac{RT(1 - e)}{V^2} (V + B) - \frac{A}{V^2} \quad (1)$$

where  $A = A_0(1 - a/V)$ .

$B = B_0(1 - b/V)$ .

$e = c/V T^3$ .

Units:  $P$  = pressure, atmospheres.

$V$  = molal volume, liters per mol.

$T$  = temperature, °Kelvin ( $= t^\circ\text{C.} + 273.16$ ).

The constants for this equation are given in Table VII.

<sup>1</sup> Beattie and Bridgeman, *Proc. Am. Acad. Arts Sciences*, 63, No. 5, p. 229-308 (1928).

TABLE VII

CONSTANTS OF THE BEATTIE AND BRIDGEMAN EQUATION OF STATE

$$R = 0.08206 \frac{(\text{atm.}) (\text{liters})}{(\text{gm. mol}) (^\circ\text{K.})}$$

Gas	$A_0$				
Helium...	0.0216	0.05984	0.01400	0.0	0.0040
Neon.....	0.2125	0.02196	0.02060	0.0	0.101
Argon....	1.2907	0.02328	0.03931	0.0	5.99
Hydrogen.	0.1975	-0.00506	0.02096	-0.04359	0.0504
Nitrogen.	1.3445	0.02617	0.05046	-0.00691	4.20
Oxygen...	1.4911	0.02562	0.04624	+0.004208	4.80
Air.....	1.3012	0.01931	0.04611	-0.001101	4.34
CO <sub>2</sub> .....	5.0065	0.07132	0.10476	0.07235	66.00
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O.	31.278	0.12426	0.45446	0.11954	33.33
C <sub>2</sub> H <sub>4</sub> ....	6.152	0.04964	0.12156	0.03597	22.68
Ammonia	2.3930	0.17031	0.03415	0.19112	476.87
CO.....	1.3445	0.02617	0.05046	-0.00691	4.20
N <sub>2</sub> O.....	5.0065	0.07132	0.10476	0.07235	66.0
CH <sub>4</sub> ....	2.2769	0.01855	0.05587	-0.01587	12.83
C <sub>2</sub> H <sub>6</sub> ....	5.8800	0.05861	0.09400	0.01915	90.00
C <sub>3</sub> H <sub>8</sub> ....	11.9200	0.07321	0.18100	0.04293	120
<i>n</i> -C <sub>4</sub> H <sub>10</sub> .	17.794	0.12161	0.24620	0.09423	350
	54.520	0.20066	0.70816	0.19179	400

An approximate form<sup>1</sup> of this equation in terms of the molal volume,  $V$ , is:

$$V = \frac{RT}{P} + \frac{\beta}{RT} + \frac{\gamma}{R^2 T^2} P + \frac{\delta}{R^3 T^3} P^2 \quad (2)$$

where  $\beta = RTB_0 - A_0 - \frac{Rc}{\pi^2}$ .

$$\gamma = -RTB_0b + A_0a - RB_0c$$

$$\delta = RB_0b \frac{c}{\pi^2}.$$

It is evident that, as the volume increases, Equation 1 approaches in form the limiting relation

$$P = \frac{RT}{V} \quad (3)$$

<sup>1</sup> *J. Am. Chem. Soc.* **49**, 1665 (1927); **50**, 3133 (1928); *Proc. Am. Acad. Arts Sci.*, **63**, 229 (1928); and *Z. Physik*, **62**, 95 (1930).

This is the equation of state for perfect gases. It is of sufficient importance to warrant discussion in a separate chapter.

### APPROXIMATION FORMULAS

Because our data are incomplete it is convenient to have methods for estimating the more important properties of matter. Although based in part on theoretical considerations, these methods are, in general, empirical. They represent certain useful correlations of experimental results, especially helpful where data are incomplete. In addition they are useful as a guide in judging the reliability of experimental results and as an aid in extrapolation.

**Vapor Pressures of Pure Liquids.** At any given temperature the vapor pressures of various pure liquids differ widely, but for most substances the curves of vapor pressure versus temperature have the same general shape. Therefore any method of plotting which gives a straight-line vapor-pressure curve for one substance will give approximately a straight line for all.

This fact was utilized by Cox<sup>1</sup> to construct the Cox chart (Figure 5) for paraffin hydrocarbons. Here water is the reference material. A straight line is drawn at some convenient angle on rectangular coordinate paper. This line is the vapor-pressure curve of water. From this and experimental data on water it is now possible to construct the appropriate scales of pressure and temperature along the coordinate axes. Usually a logarithmic scale is used for pressure. If on this diagram the data for the various hydrocarbons are plotted, substantially straight lines, intersecting at a common point, will be obtained. If the point of intersection and one value of vapor pressure for any particular hydrocarbon are known, estimation of the whole curve is possible.

On this same diagram a different group of substances, *e.g.*, the alcohols, may be plotted, and their curves will intersect at another common point. Using this intersection and one experimental point, for a given alcohol, the whole vapor-pressure curve may be estimated.

A method proposed by Dühring<sup>2</sup> is often helpful. This is also based on the fact that the vapor-pressure curves of all pure substances are of the same general shape. Temperatures being chosen where the substance in question and a reference substance have the same vapor pressures, a plot is made of the temperatures for the first against the temperatures of the reference material. If the chosen reference material is similar to the substance, practically a straight line results. Because of

<sup>1</sup> *Ind. Eng. Chem.*, 15, 592 (1923).

<sup>2</sup> "Neue Grundgesetze zur nationale Physik und Chemie," Erste Folge, Leipzig, 1878.

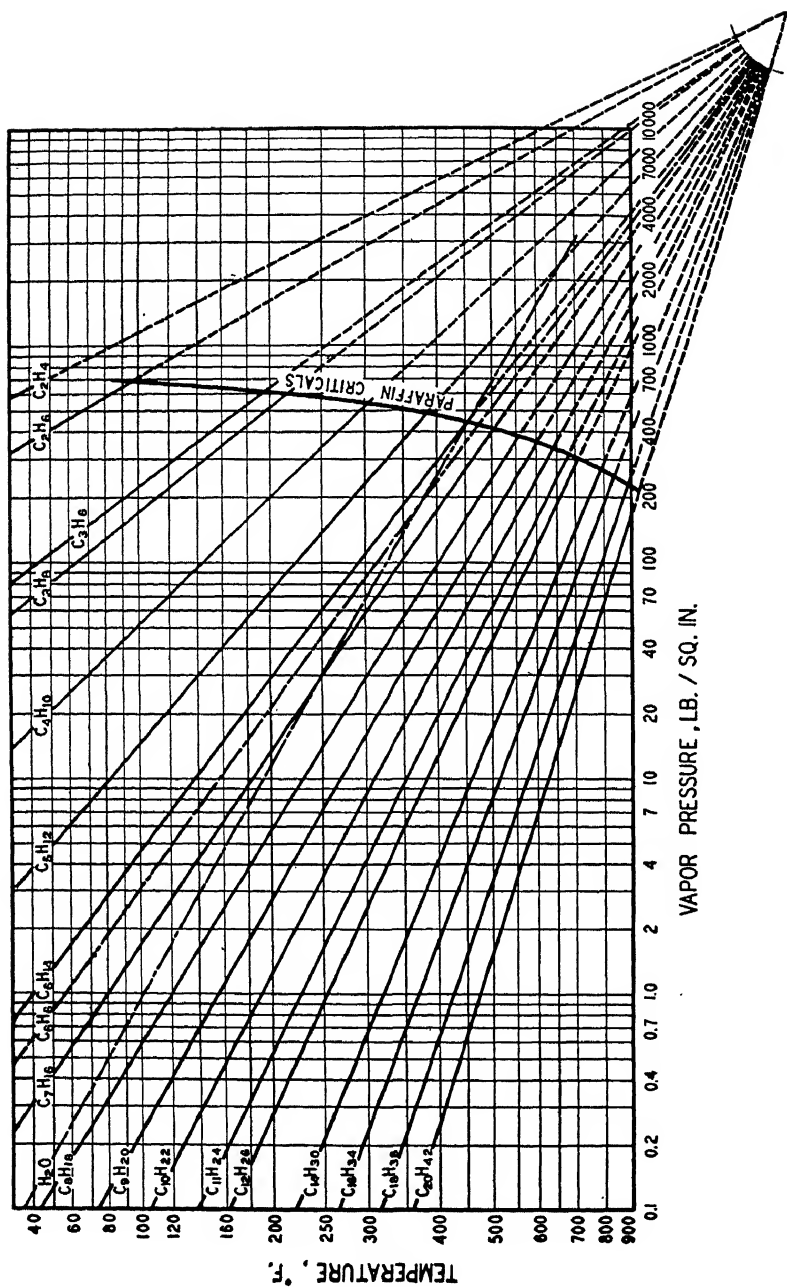


FIG. 5. Cox Chart for Hydrocarbons.

the excellent data available, water is usually taken as the reference material. Even for substances far different in chemical structure the deviation from a straight line is not great. The method is illustrated in Figure 6. Dühring's rule makes possible interpolation and extrapolation of vapor-pressure data for any substance if two points on its vapor-pressure curve are known. The method may also be used for solutions provided that the Dühring lines are constructed for fixed concentrations. Figure 7 is a plot for caustic solutions.

**Critical Constants for Pure Substances.** Several simple equations for estimating the critical conditions have been proposed and some are listed in Table VIII.

TABLE VIII  
EQUATIONS FOR ESTIMATING CRITICAL CONSTANTS

Equation	Authority
$\log \frac{P_c}{P} = \alpha \left( \frac{T_c}{T} - 1 \right) (\alpha = \text{about } 3)$	Van der Waals
$T_c = \frac{3}{2} T_{b.p.}$	Guldberg-Guye
$T_{m.p.} + T_{b.p.} = T_c$	Prud'homme
$\rho_c = \frac{1}{V_c} = 3.7 \frac{MP_c}{RT_c}$	Young ( $\rho_c$ for either vapor or liquid)

Probably the best approximation for the *critical temperature* is that proposed by Watson.<sup>1</sup>

$$\frac{T_e}{T_c} = 0.283^{0.18} \quad (4)$$

where here  $\rho_{b.p.}$  = density of liquid at boiling point, grams per cubic centimeter. The boiling point (1 atm.) being known,  $T_e$  may be obtained from Figure 8. The temperatures to be used are those based on the absolute scale, *i.e.*,

$$T^{\circ}\text{K.} = t^{\circ}\text{C.} + 273.16^{\circ}$$

For water and other so-called polar liquids Watson's rule will give incorrect results. This method also breaks down for low-boiling liquids such as hydrogen and helium.

<sup>1</sup> *Ind. Eng. Chem.*, 23, 361 (1931).

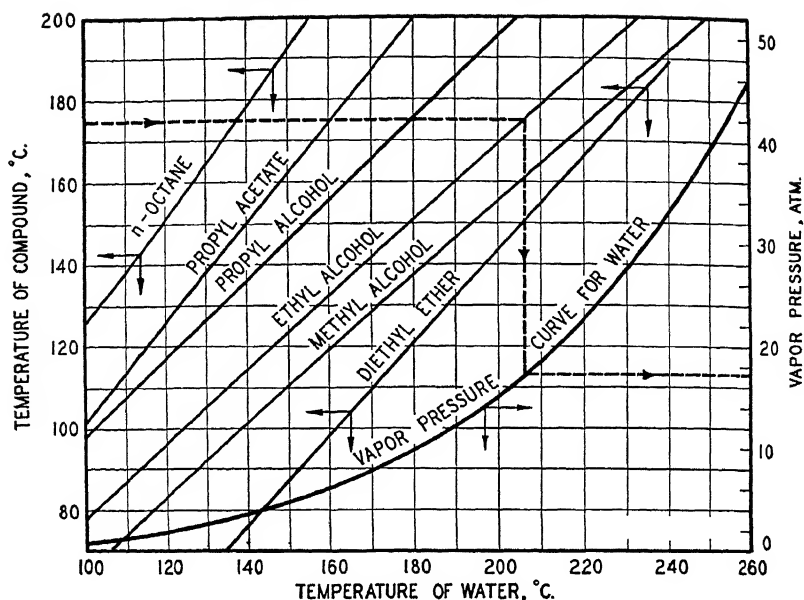


FIG. 6. Dühring Lines for Various Liquids. Based on data from the "International Critical Tables," Vol. 3, pp. 228-245.

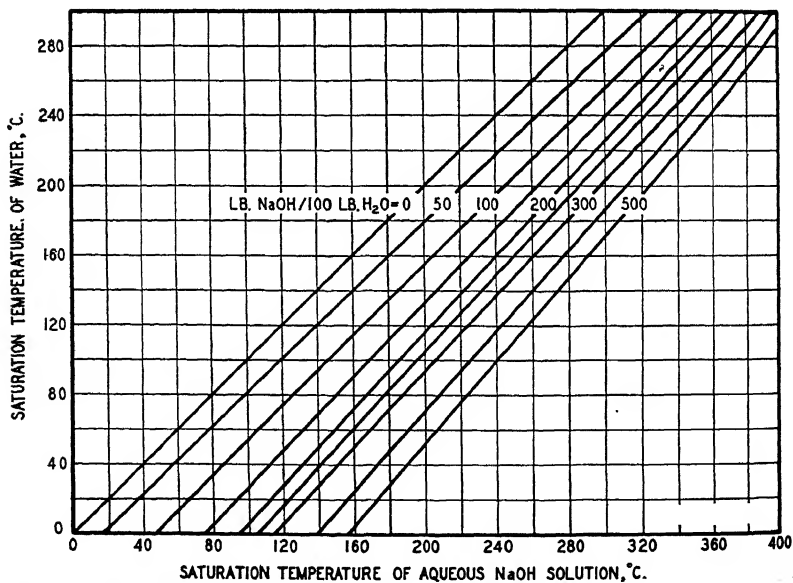


FIG. 7. Dühring Lines for Caustic Solutions. Based on data from the "International Critical Tables," Vol. 3, p. 370.

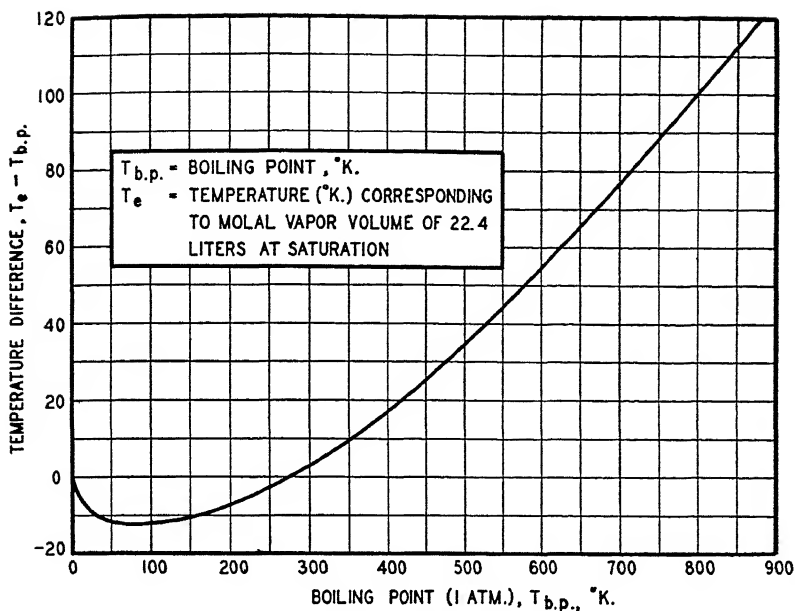


FIG. 8. Watson Plot for Estimating Critical Temperatures.

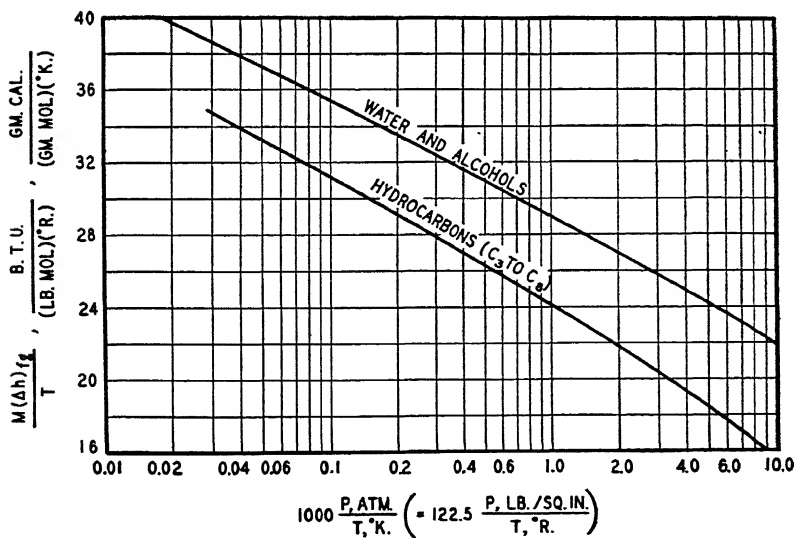


FIG. 9. Hildebrand Function for Enthalpy of Vaporization.



**Latent Heat of Vaporization — Enthalpy of Vaporization.** When exact data are lacking, Trouton's rule is often useful. At 1 atm.

$$\frac{M\Delta h_{fg}}{T_{b.p.}} = 21 \quad (5)$$

That the rule is approximate is indicated by the values in Table IX.

TABLE IX  
ENTHALPY OF VAPORIZATION AT BOILING POINT  
("International Critical Tables," Vol. 5, pages 135-137.)

Substance	$T_{b.p.}$	$M\Delta h_{fg}$	$M\Delta h_{fg}/T_{b.p.}$
	$^{\circ}\text{K.}$	gm. cal./gm. mol	gm. cal./gm. mol ( $^{\circ}\text{K.}$ )
Hydrogen . . . . .	20	109	5.35
Nitrogen . . . . .	77	1350	17.5
Methyl formate . . . . .	304	5610	18.5
Carbon tetrachloride . . . . .	350	7100	20.3
Ethyl alcohol . . . . .	351	9380	26.7
Water . . . . .	373	9703	26.0
Octane . . . . .	398	8100	20.4
Chlorobenzene . . . . .	405	8700	21.5

Hildebrand has proposed an approximation which is not limited to the heat of vaporization at 1 atm. He states that  $M\Delta h_{fg}/T$  is a function of the molal vapor concentration. On the assumption<sup>1</sup> that this is proportional to  $P/T$ , a plot may be constructed as indicated by Figure 9. On such a plot chemically similar substances will be found to fall on a single group of closely grouped lines. For any group a single line may be drawn. This has been done for two groups on Figure 9.

Another approximation applicable only at the normal boiling point is that proposed by Kistiakowsky.<sup>2</sup>

$$\frac{M\Delta h_{fg}}{T_{b.p.}} = 8.75 + 4.571 \log T_{b.p.} \quad (T = ^{\circ}\text{K.}) \quad (6)$$

Figure 10 proposed by Watson<sup>3</sup> gives relative values of  $M\Delta h_{fg}/T$  as

<sup>1</sup> Lewis and Weber, *Ind. Eng. Chem.*, 14, 485 (1922); McAdams and Morrell, *Ind. Eng. Chem.*, 16, 375 (1924).

<sup>2</sup> *Z. physik. Chem.*, 107, 65-73 (1923).

<sup>3</sup> *Ind. Eng. Chem.*, 23, 362 (1931).

ordinates against values of  $T_R$  as abscissas. The reduced temperature  $T_R$  is  $T/T_c$ , where  $T_c$  is the critical temperature. Along this curve values at any two temperatures for any compound are given by the relation:

$$\frac{\left(\frac{M\Delta h_{fg}}{T}\right)_1}{\left(\frac{M\Delta h_{fg}}{T}\right)} = \frac{\text{Ordinate at } T_1}{\text{Ordinate at } T} \quad (7)$$

From Kistiakowsky's equation the heat of vaporization at the boiling point may be calculated for any compound whose boiling point is known. If this value is used in connection with Figure 10, calculation of heat of vaporization at any other temperature is possible.

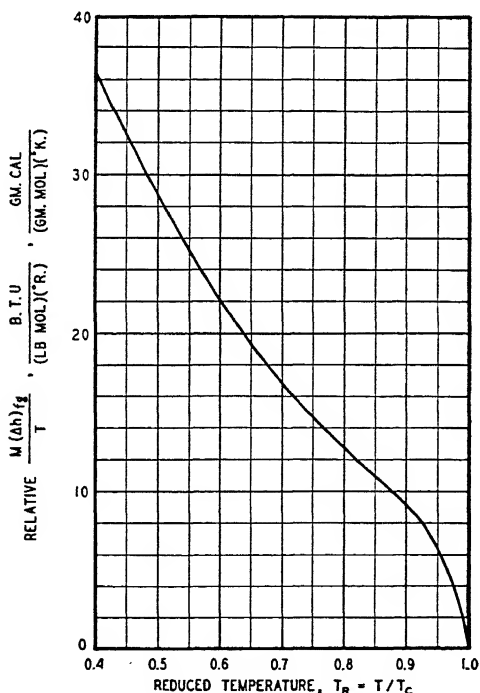


FIG. 10. Watson Function for Enthalpy of Vaporization.

**Latent Heat of Fusion — Enthalpy of Fusion.** Similar to Trouton's rule for the heat of vaporization, an approximation has been suggested for estimating the atomic enthalpy of fusion for the elements:

$$M\Delta h_{sf} = 2.2T_{m.p.} \quad (8)$$

As Table X indicates, the rule is considerably in error for many substances.

TABLE X  
ENTHALPY OF FUSION\*

Substance	$M\Delta h_{sf}$ gm. cal./gm. atom	$T_{m.p.}$ °K.	$M\Delta h_{sf}$ <sup>t</sup> m.p. gm. cal./gm. atom (°K.)
Argon . . .	268	83	23
Sulfur . . .	300	119	52
Sodium . . .	630	371	1.70
Zinc . . . . .	1595	693	30
Aluminum .	2550	932	74
Copper . . .	3110	1357	2.29

\* Kelley, U. S. Bureau of Mines, *Bulletin* 371, 1934.

#### NOTATION FOR CHAPTER VI

##### Upper Case:

$A, A_0, B, B_0$	Constants in Beattie-Bridgeman equation of state
$M$	Molecular weight
$P$	Absolute pressure
$R$	Gas constant
$T$	Absolute temperature
$V$	Volume

##### Lower Case:

$a, b, c, e$	Constants in Beattie-Bridgeman equation
$e$	Internal energy per unit mass, B.t.u./lb.
$h$	Enthalpy per unit mass, B.t.u./lb.
$s$	Entropy per unit mass, B.t.u./lb.) (°R.)
$t$	Temperature, °F. or °C.
$v$	Volume per unit mass, cu. ft./lb.

##### Subscripts:

b.p.	Boiling point (normal atmospheric)
$c$	Critical
$e$	Equivalent temperature, Equation 4
$f$	Fluid (liquid) state
$fg$	Vaporization (liquid to gas)
m.p.	Melting point
$s$	Solid state
$sf$	Melting (solid to liquid)

## PROBLEMS

*Greek letters:*

$\rho$	Density, gm./cc. or lb./cu. ft.
$\Delta$	(Final value) — (Initial value)

## PROBLEMS

1. Steam at 150 lb./sq. in. abs. pressure and superheated 200°F. is allowed to undergo a change at constant pressure until it is just dry and saturated.

(a) What were the original temperature, specific volume, internal energy and enthalpy of the steam?

(b) Per pound of steam expanded, what were the work done and the heat added?

2. A multistage turbine takes steam at 200 lb./sq. in. abs., superheated 160°F. Heat losses from the unit are negligible, and there is no reheating of the steam between stages. The exhaust steam is at 20 lb./sq. in. abs. and 0.97 quality. The small losses in the bearings being neglected, what is the steam consumption of the unit expressed as pounds of steam per horsepower-hour of shaft work?

3. A steam boiler with all valves closed and having a volumetric capacity of 1000 cu. ft. contains 500 cu. ft. of water at 70°F. How many B.t.u. will have been added to the boiler contents by the time a pressure of 200 lb./sq. in. abs. has been reached? What percentage of the boiler contents will then be steam?

4. The "throttling calorimeter," for getting the quality of wet steam, consists of a chamber fitted with a pressure gage, followed by a very small orifice leading to a second chamber containing a pressure gage and a thermometer. Steam, the quality of which is to be determined, is allowed to enter the first chamber, pass through the orifice, and then flow slowly through the second chamber. The apparatus is so constructed that the operation is practically adiabatic. Using such a device with steam originally at 50 lb./sq. in. abs. as measured in the first chamber, it is found that the temperature in the second is 180°F. when the pressure is 5 lb./sq. in. abs. What was the quality of the 50 lb./sq. in. steam? What is the lowest quality which can be determined in this device operating under the above-stated pressure conditions?

5. An insulated evacuated tank having a volumetric capacity of 50 cu. ft. is attached to a constant pressure line containing steam at 50 lb./sq. in. abs. superheated 10°F. Steam is allowed to flow slowly into the tank until the pressure has risen to 50 lb./sq. in. abs. Heat losses being neglected, and the metal of the tank being assumed to have negligible heat capacity, how many pounds of steam will have entered the tank?

6. What would have been the temperature of the steam in the tank of Problem 5 had the experiment been stopped when the pressure was 30 lb./sq. in. abs.?

7. In a certain paper mill two steam boilers are to be operated in parallel. Each has a volumetric capacity of 1000 cu. ft., and each contains 18,000 lb. of steam and water. The first boiler registers a pressure of 200 lb./sq. in. abs., but, owing to an error, it is connected to the second when the pressure in the latter is but 75 lb./sq. in. abs. What will be the pressure in the system after equilibrium has been attained, on the assumptions that no steam is withdrawn, that no heat is added to the system during the change, and that there is no interchange of heat between the boiler shells and their contents?

8. Water at 90 lb./sq. in. abs. and 300°F. is allowed to flow from a faucet into a room where the pressure is atmospheric. What is the quality of the mixture just as it leaves the faucet?

9. An experimental apparatus consisting of a coil of steel pipe (inside diameter = 2 in.) preceded by an electrically driven high-pressure pump is so arranged that pump inlet and coil outlet are at the same level. The coil may be heat insulated, heated, or cooled as desired. A control valve is placed between the pump and coil. Dry saturated steam at 100 lb./sq. in. abs. pressure is fed to the apparatus at the rate of 100 lb./hr. A series of experimental runs yields the following results (basis: 1 hour):

Heat Loss in B.t.u.		Work Input of Pump, hp-hr.	Condition at Coil Outlet Pressure	
From Pump	From Coil		lb./sq. in.	T°F.
0	0	0	20	290
0	0	1	120	377
500	2500	0	100	327.8
500	-3000	1	110	420
0	3000	0	100	327.8
546	1800	1	110	334.8

Calculate  $\Delta H$  for each run, and where possible compare the results with those read from the steam tables.

10. Referring to Problem 3, how many B.t.u. must have been added to the boiler on the assumption that, not only was the pressure raised to 200 lb./sq. in. abs., but, in addition, 10,000 lb. of dry saturated steam at 200 lb./sq. in. was withdrawn from the boiler? No water was added during the process.

11. A well-insulated vertical steam cylinder of negligible heat capacity, fitted with a piston weighing 1000 lb. and having an area of 100 sq. in., contains steam at 50 lb./sq. in. abs., superheated 10°F. The piston is held in position by a latch, and its upper surface is exposed to the atmosphere. The latch is released and the piston moves in the cylinder, eventually coming to rest because of friction. What is the final quality of the steam in the cylinder? How many pounds of steam must be in the cylinder if the piston comes to rest 5 ft. above its original position?

12. The temperature of some pieces of dry ice in a Dewar flask open to the atmosphere was measured and found to be -120°F. Criticize this statement.

13. Estimate with the aid of a CO<sub>2</sub> diagram:

- The specific heat of solid CO<sub>2</sub> at 14.7 lb. abs. and -110°F.
- The specific heat of liquid CO<sub>2</sub> at 0°F.
- The value of  $k$ ,  $Mc_p/Mc_v$ , for gaseous CO<sub>2</sub> at 100°F., and 500 lb. abs.

14. Two pounds of CO<sub>2</sub> originally in a cylinder at 80 lb./sq. in. abs. and 0°F. is to be compressed isothermally and reversibly to a final volume of 0.2 cu. ft. Calculate the heat added and the work done during this process.

15. Repeat Problem 14 on the assumption that the compression was carried out in a four-cylinder single-acting compressor operating reversibly and running at 250 r.p.m.

16. Saturated liquid CO<sub>2</sub> at 60°F. is allowed to flow through a cracked valve (Joule-Thomson expansion) to produce solid CO<sub>2</sub> at 1 atm. pressure. What yield of solid do you expect per pound of liquid expanded?

17. Two cylinders, the first of 6 cu. ft. capacity containing 60 lb. of CO<sub>2</sub>, the second of 40 cu. ft. capacity containing CO<sub>2</sub> at 300 lb./sq. in. and 80°F., are con-

nected by a valve and the contents allowed to come to equilibrium without energy exchange with the surroundings. What is the final condition of the material in the tanks?

18. A tank containing  $\text{CO}_2$  is heated until the pressure is 200 lb./sq. in. abs. and the temperature  $140^\circ\text{F}$ . This requires a heat input to the  $\text{CO}_2$  of 60 B.t.u./lb. What was the original condition of the  $\text{CO}_2$  in the tank?

19.  $\text{CO}_2$  gas originally at 600 lb./sq. in.,  $100^\circ\text{F}$ ., is expanded to 100 lb./sq. in.,  $0^\circ\text{F}$ ., by passing it through a turbine unit. It is known that the  $PV$  relationship follows the law  $PV^n = C$  very closely. In this equation  $n$  and  $C$  are constants. Per pound of gas expanded, calculate the heat which must be added to or lost from the gas, explaining in which direction the heat flows.

20. At  $18^\circ\text{C}$ . the reversible voltage for the decomposition of liquid water into dry hydrogen and oxygen gas, each at 1 atm., is 1.23 volts, and the heat of formation of liquid water from the gaseous elements at 1 atm. is 286.2 kilojoules per gram mol of water. Assuming these data correct, calculate the rate of heat supply (B.t.u./hr./cell) to keep the cells of the bank described below at  $18^\circ\text{C}$ .

Data:

Number of cells in bank, 30.

Voltage across bank, 60.

Current, 350 amperes.

Pressure in  $\text{H}_2$  and  $\text{O}_2$  mains, 150 lb. abs.

Pressure drop due to valves, etc., between cell and mains, 10 lb./sq. in.

Current efficiency assumed 100 per cent.

## CHAPTER VII

### PERFECT GASES

**The Perfect Gas Law.** At low pressures and elevated temperatures and in the absence of chemical reaction, all gases and vapors approach a condition such that their  $P$ - $V$ - $T$  properties may be expressed by a simple algebraic equation of state. Historically this equation was developed as a result of a series of extended experimental investigations. The general law was preceded by two more restricted formulations: first, the law of Boyle and Mariotte, that for a fixed weight of given gas the product of pressure and volume,  $PV$ , is constant at constant temperature; and second, the law of Charles and Gay-Lussac, that at constant pressure the volume is directly proportional to the absolute temperature. These combined statements are represented by the equation

$$PV = RT \quad (1)$$

From an experimental viewpoint absolute zero is the value  $-273.16^{\circ}\text{C}$ . determined with the aid of a gas thermometer by constant density extrapolation of gas pressure versus temperature to zero pressure. Temperatures referred to this figure as a datum are called absolute. Common temperature scales (Centigrade and Fahrenheit) have neither the same datum nor the same number of subdivisions between the fixed points (freezing and boiling of water under normal atmospheric pressure). Absolute temperature scales do have the same datum, but different numerical values at any chosen fixed point, *e.g.*, melting point of sulfur. As a result, two absolute scales, the Kelvin and the Rankine, are in general use.

$$\begin{aligned} T^{\circ}\text{ Kelvin} &= t^{\circ}\text{ Centigrade} + 273.16 \\ T^{\circ}\text{ Rankine} &= t^{\circ}\text{ Fahrenheit} + 459.69 \end{aligned}$$

The above relation includes everything formally designated by the expression "gas laws." However, by slight modification it is possible to arrive at an expression more convenient for general use. For the relation given, values of  $PV/T$  (and hence  $R$ ) are not the same for unit masses of different gases. If the gas law is written

$$PV = NRT \quad (2)$$

where  $N$  is the number of mols (molecular weights) of gas, the value of  $R$  will be the same for all gases in any chosen system of units.

Provided that the perfect gas law applies, the molecular weight of a material may be defined as the weight in grams of 22.4 liters at 0°C. and 1 atm. or, what is equivalent, the weight in pounds of 359 cu. ft., under the same conditions. The conditions are often referred to as standard conditions (S.C.). The molecular weight in grams is a gram mol; in pounds, a pound mol. In a restricted sense they are units of gas volume under specified conditions of temperature and pressure.

Values of  $R$  commonly used are listed in Table I.

TABLE I  
VALUES OF  $R$  FOR  $PV = NRT$

$R$	Units of $R$ ( $= PV/NT$ )
82.06	(atm.) (cc.)/(gm. mol) (°K.)
0.08206	(atm.) (liters)/(gm. mol) (°K.)
1.987	(gm. cal.)/(gm. mol) (°K.)
1.987	(B.t.u.)/(lb. mol) (°R.)
1.987	(C.h.u.)/(lb. mol) (°K.)
1546	(lb./sq. ft.) (cu. ft.)/(lb. mol) (°R.)

**Conditions Influencing Validity of Gas Laws.** Although no real gases follow the gas law quantitatively, deviations are small under some conditions. This is true for all gases if (1) the pressures are moderate and the temperatures are above the critical, (2) the pressures are low (a few atmospheres) even though the temperatures may be less than the critical. For most engineering purposes, use of the gas laws up to pressures of 10 to 20 atm. does not introduce serious error if absolute temperatures are at least twice the critical. Below the critical temperature these errors may be neglected up to 1 atm., although for saturated vapors they may be as much as 3 to 5 per cent.

**Energy Relations of Perfect Gases.** Joule and Thomson discovered the fundamental fact relative to the energy characteristics of perfect gases. They expanded ordinary gases adiabatically under conditions of steady flow through a restricted passage (Joule-Thomson porous plug expansion). These experiments indicated that, for any gas under conditions where the gas law is valid, the temperature change during such an expansion is zero. The experiments are so conducted that (a) velocity effects and changes in height are negligible, (b) no net or shaft mechanical work is done by the gas on the surroundings, and (c) conditions are adiabatic.

For a steady flow process

$$X_1 + E_1 + P_1 V_1 + \frac{U_1^2}{2g} + Q - W_{\text{shaft}} = X_2 + E_2 + P_2 V_2 + \frac{U_2^2}{2g} \quad (3)$$



But for the Joule-Thomson process, the above equation simplifies to  $\Delta E + \Delta PV = 0$ . Since for a perfect gas the temperature does not change and therefore the  $PV$  product remains constant, there can be no change in internal energy. In a Joule-Thomson expansion of a *perfect gas* there is no change in either temperature or internal energy. Since the pressure does change during expansion, the internal energy is independent of the pressure, *i.e.*,  $(\partial E / \partial P)_T = 0$ . The condition of the gas is determined by its pressure and temperature; therefore, the **internal energy of a perfect gas is a function of its temperature only, independent of pressure and volume.** The energy characteristics of a perfect gas may, accordingly, be expressed by the equation  $dE = NM c_v dT$ . Since here  $E$  is a function of temperature only,  $c_v$  must also be a function of temperature only. Moreover,  $\Delta H = \Delta E + \Delta(PV)$  and for a given perfect gas  $\Delta(PV)$  depends on temperature only. Therefore  $\Delta H$  must be a function of temperature only. But for a constant-pressure process  $dH = M c_p dT$ . For any perfect gas, change in enthalpy will be  $dH = M c_p dT$ . The enthalpy is not a function of the pressure.

Thus for a perfect gas not only is the relation

$$PV = NRT$$

valid, but in addition the internal energy depends on the temperature only. Later discussion will prove that these two relations are not independent.

Instead of the experimental approach here presented, mathematically it could be stated that, by definition for a group of imaginary substances: (1)  $PV = NRT$ ; (2) the internal energy is a function of temperature only. The experimental presentation, although perhaps not so concise, seems more satisfactory.

**Relation Between the Two Heat Capacities.** Let  $N$  mols of perfect gas be heated and expanded reversibly at constant pressure. This may be assumed to occur in a cylinder fitted with a frictionless piston. By the first law

$$dQ = dE + dW$$

Also for this process

$$dQ = NM c_p dT$$

$$dE = NM c_v dT$$

$$dW = P dV$$

$$P dV = NR dT$$

Therefore

$$\begin{aligned} NM c_p dT &= NM c_v dT + NR dT \\ R &= M c_p - M c_v \end{aligned} \quad (4)$$

By definition, for any gas,  $k = c_p/c_v$ . For perfect gases, if two of the three quantities,  $M c_p$ ,  $M c_v$ , or  $R$ , are known, the other may be calculated

$$M c_v = \frac{R}{k-1}; \quad M c_p = \frac{Rk}{k-1} \quad (5)$$

### ENERGY EFFECTS FOR TYPICAL GAS CHANGES

**Reversible Isothermal Changes.** The reversible non-flow work is  $W = \int P dV$ . Here  $P = NRT/V$  and

$$W = NRT \int \frac{dV}{V} = NRT \ln \frac{V_2}{V_1} \quad (6)$$

For this constant temperature change,  $PV$  is a constant and therefore

$$W = NRT \ln \frac{P_1}{P_2} \quad (7)$$

The reversible shaft work for processes where there are mechanical effects only,  $-\int V dP$ , results in the same expression. This may readily be visualized by plotting on a  $PV$  plane. The non-flow work is represented by area  $FBCE$  (Figure 1); the flow work, by area  $ABCD$ . Since the  $PV$  product is constant the areas under lines  $DC$  and  $AB$  are equal although they represent work effects having opposite signs. Therefore  $\text{area } FBCE = \text{area } ABCD$ . Since in an isothermal change for perfect gases  $\Delta E = 0$ , it follows that for isothermal non-flow cases

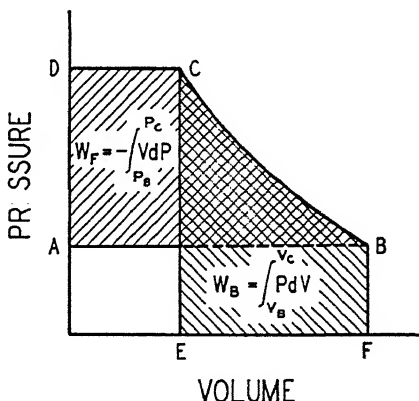


FIG. 1. Pressure-Volume Relations for Gas Compressor without Clearance.

$$Q - W = 0 \quad (8)$$

while for flow cases

$$Q - W = \Delta \frac{U^2}{2g} + \Delta X \quad (9)$$

**Reversible Adiabatic Changes.** In an adiabatic non-flow change, since  $dQ = 0$ ,  $dE = -dW$ . If the change is reversible,  $dE = -P dV$ . This expression is not integrable directly because it contains three variables, but for a perfect gas either  $P$  or  $dV$  may be eliminated. Remember that  $PV = NRT$  and  $dE = Mc_v dT$ . Therefore

$$\int \frac{Mc_v dT}{T} = R \ln \frac{V_1}{V_2} = R \ln \frac{P_2 T_1}{P_1 T_2} \quad (10)$$

Two important cases will be considered in evaluating the last expression.

For the first,  $Mc_v$  is assumed constant over the temperature range in question. Integrating,

$$R \ln \frac{V_1}{V_2} = Mc_v \ln \frac{T_2}{T_1} \quad \text{or} \quad \frac{V_1}{V_2} = \left( \frac{T_2}{T_1} \right)^{Mc_v/R} \quad (11)$$

But 
$$\frac{R}{Mc_v} = k - 1, \quad \text{whence} \quad \left( \frac{V_1}{V_2} \right)^{k-1} = \frac{T_2}{T_1} \quad (12)$$

Eliminating  $T$ ,

$$P_2 V_2^k = P_1 V_1^k \quad (13)$$

This expression is valid only for *reversible adiabatic changes of perfect gases*.

For non-flow work

$$\begin{aligned} W &= -\Delta E = -NMc_v \Delta T = -\frac{NR}{k-1} \Delta T \\ &= -\frac{\Delta(PV)}{k-1} = \frac{NRT_1}{k-1} \left[ 1 - \left( \frac{P_2}{P_1} \right)^{(k-1)/k} \right] \\ &= \frac{P_1 V_1}{k-1} \left[ 1 - \left( \frac{P_2}{P_1} \right)^{(k-1)/k} \right] \end{aligned} \quad (14)$$

For *adiabatic flow* operation, in the absence of potential and kinetic energy effects,  $W_{\text{shaft}} = -\Delta H = -N \int Mc_p dT$ . If the change is reversible and only mechanical effects are of importance, this equals  $-\int V dP$ . Integrated as before, the relations between initial and final values of  $P$ ,  $V$ , and  $dT$  are unchanged, but the work becomes

$$\begin{aligned} W_{\text{shaft}} &= -NMc_p \Delta T = -\frac{k}{k-1} \Delta(PV) \\ &= \frac{kNRT_1}{k-1} \left[ 1 - \left( \frac{P_2}{P_1} \right)^{(k-1)/k} \right] \end{aligned}$$

For the second case  $Mc_p$  is assumed linear in  $T$ ;  $Mc_p = a + bT$ . Substituting in Equation 10,

$$R \ln \frac{V_1}{V_2} = a \ln \frac{T_2}{T_1} + b(T_2 - T_1) \quad (16)$$

or

$$R \ln \frac{P_2}{P_1} = (a + R) \ln \frac{T_2}{T_1} + b(T_2 - T_1) \quad (17)$$

Then

$$W = N \left[ a(T_1 - T_2) + \frac{b}{2} (T_1^2 - T_2^2) \right] \quad (18)$$

or

$$W_{\text{shaft}} = N \left[ (a + R)(T_1 - T_2) + \frac{b}{2} (T_1^2 - T_2^2) \right] \quad (18a)$$

Where  $T_1$  and  $T_2$  are known, these equations may be solved directly; otherwise solution by trial and error is often necessary. This is likewise true in the general case where  $Mc_p$  is a more complicated function of  $T$ .

**Comparison of Isothermal and Adiabatic Reversible Work Effect.** Some study will lead to the conclusion that differences between the work effects for adiabatic and isothermal changes decrease with decreasing values of  $k$ , *i.e.*, as the heat capacities increase. But even for large values of  $k$  the differences in work effects between the two become smaller as the ratio of final to initial pressures,  $P_2/P_1$ , approaches unity. This pressure ratio is called the compression (or expansion) ratio.

**Polytropic Changes.** A study of actual compressions and expansions shows that frequently their curves can be approximated by equations of the type

$$PV^n = C \quad (19)$$

where  $n$  is a constant for any given change.  $n$  is not equal to  $k$  but may have values ranging from less than 1 to greater than  $k$ . Such changes are called polytropic.<sup>1</sup>

<sup>1</sup> Although discussion is here limited to perfect gases, often an equation of the form  $PV^n = C$  is found adequately to express the pressure-volume relations during certain types of changes for vapors to which the gas laws may not be applied without considerable error. Expansion of steam in an engine cylinder offers a good example.

If reversibility and the gas law may be assumed,

$$\begin{aligned}
 W &= \int P \, dV \\
 dQ &= dE + P \, dV \\
 &= NM c_v \, dT + P \, dV \\
 &= NM c_v \, dT + C \frac{dV}{V^n}
 \end{aligned} \tag{20}$$

Because of the fortuitous separation of variables this equation integrates between limits to

$$\begin{aligned}
 Q &= N \int M c_v \, dT - \frac{C}{(n-1)V^{n-1}} \Bigg|_1^2 \\
 &= N \int M c_v \, dT - \frac{PV}{n-1} \Bigg|_1^2
 \end{aligned} \tag{22}$$

$$= N \int M c_v \, dT - \frac{NRT}{n-1} \Bigg|_1^2 \tag{23}$$

If  $c_v$  is constant, then

$$\begin{aligned}
 Q &= N \left[ M c_v (T_2 - T_1) - R \left( \frac{T_2 - T_1}{n-1} \right) \right] \\
 W &= \frac{-\Delta(PV)}{n-1} = -\frac{NR\Delta T}{n-1}
 \end{aligned} \tag{25}$$

The analogy in form to the equations for adiabatic operation is obvious.

For constant  $c_v$  the heat  $Q$  is proportional to the temperature change. This characteristic is often used to define polytropic operation, but this and the previous definitions are not equivalent for variable  $M c_v$ . For constant  $c_v$

$$Q = NM c_v \Delta T = N \left( M c_v \Delta T - \frac{P \Delta V}{n-1} \right) \tag{26}$$

$$c_e = c_v \frac{n-k}{n-1} \tag{27}$$

The constant  $c_e$  is sometimes termed the "polytropic heat capacity."

For reversible *flow operations* when  $c_v$  is constant and potential and velocity effects are negligible, provided that all work effects are

mechanical,

$$W_{\text{shaft}} = -\frac{\Delta(PV)}{n-1} - \Delta(PV) = \frac{-n}{n-1} \Delta(PV) \quad (28)$$

$$= \frac{-NR\Delta T}{n-1} - \Delta(PV) = \frac{-n}{n-1} R\Delta T \quad (29)$$

$$= \frac{-n}{n-1} NRT_1 \left[ \left( \frac{P_2}{P_1} \right)^{(n-1)/n} - 1 \right] \quad (30)$$

$$\Delta H = \int C_p dT = \left( \frac{k}{k-1} \right) P_1 V_1 \left[ \left( \frac{P_2}{P_1} \right)^{(n-1)/n} - 1 \right] \quad (31)$$

Table II is a summation of various formulas for perfect gases.

**Perfect Gas Mixtures.** The first fundamental fact concerning perfect gas mixtures is that the total (mixture) pressure is equal to the sum of the partial pressures each gas in the mixture would exert were it present alone at mixture volume and temperature. Mathematically,

$$p_1 + p_2 + \cdots = \sum p = \pi \quad (32)$$

where  $p_1$ ,  $p_2$ , etc. = pressures various gases would exert at mixture volume  $V$  and mixture temperature  $T$ , and  $\pi$  = total pressure on the mixture. This is Dalton's law.

Amagat's law is a statement that the volume of a gaseous mixture is the sum of the partial volumes of the constituents each measured at the mixture pressure and temperature.

$$v_1 + v_2 + \cdots = \sum v = V \quad (33)$$

For perfect gases this follows from Dalton's law, but for non-perfect gas mixtures the two are not equivalent. The calculations for the usual volumetric gas analysis are based on the assumption that Amagat's law holds.

**Energy Relations for Perfect Gas Mixtures.** The second fundamental fact regarding perfect gas mixtures is that any two perfect gases at the same temperature blending adiabatically without chemical reaction undergo no temperature change. This assumes potential and kinetic energy effects to be negligible. For such a change  $\Delta H = 0$  and  $PV = C$ . Therefore, the internal energy of a mixture of perfect gases is the sum of those for the pure components at the same temperature. The internal energy of a perfect gas mixture, like that of a single gas, is a function of temperature only.

For non-flow mixing of perfect gases at *constant total volume*, whatever

TABLE II

## SUMMARY OF FORMULAS FOR PERFECT GASES

Notation:  $P$  = abs. pres.  $T$  = abs. temp.  $V$  = volume.  $C_p$  = molal heat capacity at constant pressure.  $C_v$  = molal heat capacity at constant volume.  $k = C_p/C_v$ .  $\Delta$  = final value - initial value.  
 Subscript: 1 = initial state; 2 = final state.  $N$  = number of mols.  $R$  = gas constant.  
 Conditions:  $PV = NRT$  for equation of state.  $C_p$  and  $C_v$  are constant.  $C_p - C_v = R$ . For flow,  $\Delta(U^2/2g)$  and  $\Delta X$  are assumed negligible.

Condition of Restraint	$V = C$	$P = C$	$T = C$	$Q = 0$ Reversible; adiabatic	$Q = C_v \Delta T$ Reversible; polytropic
$P$ - $V$ Relations	$V_1 = V_2$	$P_1 = P_2$	$P_1 V_1 = P_2 V_2$ $\frac{P_2}{P_1} = \frac{V_1}{V_2}$	$P_1 V_1^k = P_2 V_2^k$ $\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^k$	$P_1 V_1^n = P_2 V_2^n$ $\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^n$
$P$ - $T$ Relations	$\frac{P_2}{P_1} = \frac{T_2}{T_1}$	.....	$T_1 = T_2$	$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}}$	$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}}$
$T$ - $V$ Relations	.....	$\frac{V_2}{V_1} = \frac{T_2}{T_1}$	.....	$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{k-1}$	$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{n-1}$
$\Delta(PV)$	$= V(P_2 - P_1)$	$= P(V_2 - V_1)$ $= P V_1 \left(\frac{T_2}{T_1} - 1\right) = 0$	$= 0$	$= P_1 V_1 \left[\left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}} - 1\right]$ $= NRT_1 \left[\left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}} - 1\right]$	$= P_1 V_1 \left[\left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}} - 1\right]$ $= NRT_1 \left[\left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}} - 1\right]$
$\Delta T$	$= T_1 \left(\frac{P_2}{P_1} - 1\right)$	$= T_1 \left(\frac{V_2}{V_1} - 1\right) = 0$	$= 0$	$= T_1 \left[\left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}} - 1\right]$ $= T_1 \left[\left(\frac{V_1}{V_2}\right)^{k-1} - 1\right]$	$= T_1 \left[\left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}} - 1\right]$ $= T_1 \left[\left(\frac{V_1}{V_2}\right)^{n-1} - 1\right]$

$Q$	$= \Delta E = NC_v \Delta T$ $= \frac{\Delta(PV)}{k-1}$	$= \Delta H = NC_p \Delta T$ $= \frac{k}{k-1} \Delta(PV)$	$= -NRT \ln \frac{P_2}{P_1}$ $= -NRT \ln \frac{V_1}{V_2}$	$= 0$	$= \frac{-(k-n)}{(k-1)(n-1)} NR \Delta T$ $= \frac{-(k-n)(NRT_1)}{(k-1)(n-1)} \left[ \left( \frac{P_2}{P_1} \right)^{\frac{n-1}{n}} - 1 \right]$ $= \frac{-(k-n)}{(k-1)(n-1)} \Delta(PV)$ $= \frac{-(k-n)(P_1 V_1)}{(k-1)(n-1)} \left[ \left( \frac{P_2}{P_1} \right)^{\frac{n-1}{n}} - 1 \right]$
$W_{\text{non-flow}} = \int P dV$ Reversible	$= 0$	$= \Delta(PV)$ $= P(V_2 - V_1)$	$= -NRT \ln \frac{P_2}{P_1}$ $= -NRT \ln \frac{V_1}{V_2}$	$= -\Delta E = -NC_v \Delta T$ $= \frac{-NRT_1}{k-1} \left[ \left( \frac{P_2}{P_1} \right)^{\frac{k-1}{k}} - 1 \right]$ $= \frac{-\Delta(PV)}{k-1}$ $= \frac{-P_1 V_1}{k-1} \left[ \left( \frac{P_2}{P_1} \right)^{\frac{k-1}{k}} - 1 \right]$	$= \frac{-NR \Delta T}{n-1}$ $= \frac{-NRT_1}{n-1} \left[ \left( \frac{P_2}{P_1} \right)^{\frac{n-1}{n}} - 1 \right]$ $= \frac{-\Delta(PV)}{n-1}$ $= \frac{-P_1 V_1}{n-1} \left[ \left( \frac{P_2}{P_1} \right)^{\frac{n-1}{n}} - 1 \right]$
$W_{\text{shaft}} = -\int V dP$ Reversible	$= V(\Delta P) = V(P_2 - P_1) = 0$		$= -NRT \ln \frac{P_2}{P_1}$ $= -NRT \ln \frac{V_1}{V_2}$	$= -\Delta H = -NC_p \Delta T$ $= \frac{-kNRT_1}{k-1} \left[ \left( \frac{P_2}{P_1} \right)^{\frac{k-1}{k}} - 1 \right]$ $= -\frac{k}{k-1} \Delta(PV)$ $= \frac{-kP_1 V_1}{k-1} \left[ \left( \frac{P_2}{P_1} \right)^{\frac{k-1}{k}} - 1 \right]$	$= -\frac{n}{n-1} NR \Delta T$ $= \frac{-nNRT_1}{n-1} \left[ \left( \frac{P_2}{P_1} \right)^{\frac{n-1}{n}} - 1 \right]$ $= -\frac{n}{n-1} \Delta(PV)$ $= \frac{-nP_1 V_1}{n-1} \left[ \left( \frac{P_2}{P_1} \right)^{\frac{n-1}{n}} - 1 \right]$

TABLE II (Continued)

## SUMMARY OF FORMULAS FOR PERFECT GASES

Notation: $P$ = abs. pres. $T$ = abs. temp. $V$ = volume. $C_p$ = molal heat capacity at constant pressure. $C_v$ = molal heat capacity at constant volume. $k = C_p/C_v$ . $\Delta$ = final value - initial value. Subscript: 1 = initial state; 2 = final state. $N$ = number of moles. $R$ = gas constant. Conditions: $PV = NKT$ for equation of state. $C_p$ and $C_v$ are constant. $C_p - C_v = R$ . For flow, $\Delta(U^2/2g)$ and $\Delta X$ are assumed negligible.					
Condition of Restraint	$V = C$	$P = C$	$T = C$	$Q = 0$ Reversible; adiabatic	$Q = C_v\Delta T$ Reversible; polytropic
$\Delta E$	$= NC_v\Delta T$ $= \frac{\Delta(PV)}{k-1}$	$= NC_p\Delta T$ $= \frac{\Delta(PV)}{k-1}$	$= 0$	$= -W_{\text{non-flow}} = NC_v\Delta T$ $= \frac{NRT_1}{k-1} \left[ \left( \frac{P_2}{P_1} \right)^{\frac{k-1}{k}} - 1 \right]$ $= \frac{\Delta(PV)}{k-1}$ $= \frac{P_1V_1}{k-1} \left[ \left( \frac{P_2}{P_1} \right)^{\frac{k-1}{k}} - 1 \right]$	$= \frac{NRT_1}{k-1}$ $= \frac{NRT_1}{k-1} \left[ \left( \frac{P_2}{P_1} \right)^{\frac{n-1}{n}} - 1 \right]$ $= \frac{\Delta(PV)}{k-1}$ $= \frac{P_1V_1}{k-1} \left[ \left( \frac{P_2}{P_1} \right)^{\frac{n-1}{n}} - 1 \right]$
$\Delta H$	$= NC_p\Delta T$ $= \frac{k}{k-1} \Delta(PV)$	$= NC_p\Delta T$ $= \frac{k}{k-1} \Delta(PV)$	$= 0$	$= -W_{\text{shaft}} = NC_p\Delta T$ $= \frac{kNRT_1}{k-1} \left[ \left( \frac{P_2}{P_1} \right)^{\frac{k-1}{k}} - 1 \right]$ $= \frac{k}{k-1} \Delta(PV)$ $= \frac{kP_1V_1}{k-1} \left[ \left( \frac{P_2}{P_1} \right)^{\frac{k-1}{k}} - 1 \right]$	$= \frac{k}{k-1} NRT_1$ $= \frac{kNRT_1}{k-1} \left[ \left( \frac{P_2}{P_1} \right)^{\frac{n-1}{n}} - 1 \right]$ $= \frac{k}{k-1} \Delta(PV)$ $= \frac{kP_1V_1}{k-1} \left[ \left( \frac{P_2}{P_1} \right)^{\frac{n-1}{n}} - 1 \right]$



the initial temperatures and pressures of the individual components, the final condition is determined by the relation,  $\Delta E = 0$ , or

$$\sum \int_{T_0}^T NM c_v dT = \int_{T_0}^{T_m} \sum NM c_v dT, \quad (34)$$

where  $T_m$  is the mixture temperature,  $N$  the number of mols of any component,  $M$  its molecular weight,  $c_v$  its heat capacity at constant volume,  $T$  its temperature before mixing, and  $T_0$  an arbitrary datum temperature. The summation sign ( $\sum$ ) indicates the addition of all these terms for the various components of the mixture. If the heat capacities are temperature functions integration must be conducted accordingly.

Adiabatic mixing under conditions of *steady flow*, whatever the initial pressures and temperatures, or non-flow mixing at *constant pressure* is determined by the relation,  $\Delta H = 0$ , *i.e.*,

$$\sum \int_{T_0}^T NM c_p dT = \int_{T_0}^{T_m} \sum NM c_p dT \quad (35)$$

**Adiabatic Mixing of Gases Having Constant and Equal Molal Heat Capacities.** An important special case of adiabatic mixing is that in which, over the range involved,  $M c_v$  and  $M c_p$  are substantially constant, and the same for all gases involved. With these limitations, the fundamental equation,  $dE = NM c_v dT$  integrates to

$$E = NM c_v T \quad (36)$$

in which the constant of integration is arbitrarily assumed zero. Substituting  $PV/R$  for  $NT$ ,  $M c_p - M c_v$  for  $R$ , and  $k$  for  $c_p/c_v$ , this may be written

$$E = \frac{PV}{k-1} \quad (37)$$

Similarly,

$$H = NM c_p T = \frac{kPV}{k-1} \quad (38)$$

From these relations it is seen that, on mixing adiabatically two such perfect gases at constant pressure, the volumes are additive, irrespective of the initial temperatures of the gases mixed. Similarly, for adiabatic mixing at constant total volume, the pressure is

$$\pi = \frac{\sum(PV)}{\sum V} = \frac{\sum NRT}{\sum V} \quad (39)$$

Mixing at constant total volume when the pressures of the initial bodies of the gas are the same involves no change in the pressure, whatever the initial temperatures. These relations are important because they simplify many chemical calculations, but they must be used only where the molal heat capacities of the different gases are equal and constant.

**Reciprocating Gas Compressors.** Compression, without chemical reaction, of gases to pressures of a few atmospheres is an important step in many industrial processes. Practically always this is done in reciprocating gas compressors. Analysis of the operation of these machines affords an excellent opportunity to apply many of the perfect gas relations presented earlier in this chapter.

**Compressor Details.** From the viewpoint of this discussion the compressor cylinder with its piston and associated valve mechanism is of more interest than the other parts. These cylinders may be **single acting**, open at one end and capable of delivering one compression stroke per cycle; or **double acting**, where each cylinder gives two compression strokes per cycle. Often water jackets or fins are provided for cooling. To prevent the piston from striking the **cylinder head** a small clearance must be left between piston and head when the piston is at the end of its travel. **Clearance** is usually reported as percentage of stroke, *i.e.*,

$$\left( \frac{\text{Cylinder length} - \text{Piston travel}}{\text{Piston travel}} \right) (100) = \% \text{ clearance}$$

The cylinder diameter is the **bore**, and the piston travel is the **stroke**. Clearance is important, as too little leads to mechanical difficulties and too much causes loss in capacity. Capacity of air compressors is usually given in terms of **free air** (air under conditions just outside the inlet valve).

Compressor valves are usually operated solely by a difference in pressure across the two valve surfaces. Usually the valves are of extremely light weight and are held in place by weak springs.

When considerable pressures are to be obtained (more than 4 atm. for air), **staging** is often practiced. For this purpose the compressor is built with a low-pressure cylinder, followed by one or several higher-pressure cylinders. As the gas passes from the cylinder of one stage to that of the next, it practically always flows through some type of **intercooler**. In this, for the ideal case, the gas would be cooled at constant pressure to the temperature it had before entrance to the compression unit. Staging reduces work required for compression and cost of mechanical construction, especially in larger units. Even in such small units as garage compressors it is usually considered worth while. The **compression ratio** (ratio of pressure after compression to that

before) is usually made the same in all stages. For very high pressures as many as four stages are not unusual. For such a range the gas laws are not applicable.

**Pressure-Volume Relations.** A plot of pressure-volume relations in the cylinder of a compressor is a distinct aid in following the cycle of processes. Figure 2 is a somewhat idealized pressure-volume history of the gas as it passes through the cylinder.<sup>1</sup> It is representative of changes in a single-acting cylinder.

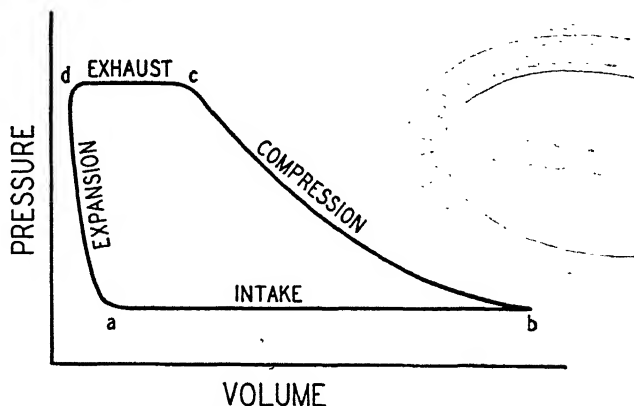


FIG. 2. Smoothed Indicator Diagram for a Gas Compressor.

The line  $ab$  represents the intake of gas into the cylinder as the piston moves outward, thus increasing the volume of the cylinder space. At point  $b$  the piston reaches the end of its stroke and starts to return. The reversal of gas flow through the intake valve automatically closes the valve, and all gas in the cylinder at point  $b$  is unable to escape. The moving piston compresses the gas along the curve  $bc$  and the pressure rises until it is slightly above that in the discharge line. This lifts the discharge valve, allowing the gas in the cylinder to start escaping into the discharge line. The instant the valve opens, escape of gas through it causes a sudden drop in the cylinder pressure. This results in the pressure oscillations indicated in Figure 3, but these soon cease and the cylinder pressure drops to that in the discharge line, plus the small friction drop through discharge valves and ports. Some gas necessarily remains in the clearance space of the compressor after closure of the discharge valve at the end of the stroke. The trapped gas expands on the return stroke of the piston until the pressure falls sufficiently to permit the intake to open. This opening may be accompanied by pressure

<sup>1</sup> This plot is often called a card or an indicator card. Indicators are discussed in the chapter on steam engines and turbines.

oscillations similar to those previously described. Actually, because of mechanical limitations, pressure-volume relations are more like Figure 4 than Figure 2.

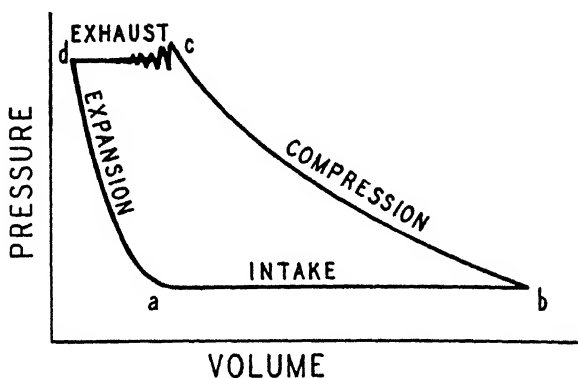


FIG. 3. Indicator Card for a Compressor Showing Oscillations in Exhaust Valve.

It is well to remember that the diagram does not actually represent conditions for a fixed amount of gas. It represents a cycle of operation, but not a cycle in a thermodynamic sense. The quantity of gas is increasing progressively along the line  $ab$ , and decreasing along  $cd$ . If

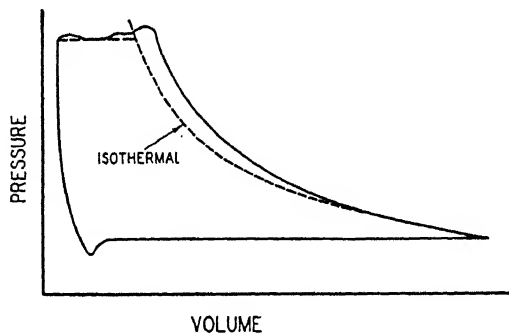


FIG. 4. Typical Indicator Card for a Gas Compressor.

the piston and valves are tight, the gas in the cylinder is constant, although not the same, along the paths  $bc$  and  $da$ . Each of these last two can be considered as giving the history of a thermodynamic system. The area enclosed by the four paths is proportional to the net work done by the piston on the gas per cycle of compressor operation. It is customary to construct only the major lines and curves of the diagram, *i.e.*, smoothing them by omitting such disturbing factors as the pressure oscillations connected with valve operation (Figure 3). This simplification usually introduces but small error.

## NOTATION FOR CHAPTER VII

*Upper Case:*

$C$	Constant
$E$	Internal energy
$H$	Enthalpy ( $= E + PV$ )
$M$	Molecular weight
$N$	Mols
$P$	Absolute pressure
$Q$	Heat added
$R$	Gas constant, Table I
$T$	Absolute temperature, °K., °R.
$U$	Average velocity
$V$	Volume
$W$	Work done by system on surroundings
$X$	Height above datum plane

*Lower Case:*

$a, b$	Constants in Equations 16-18
$c$	Heat capacity per unit mass
$g$	Gravitational acceleration, 32.2 ft./ (sec.) <sup>2</sup>
$k$	Ratio of $C_p$ to $C_v$ (or $Mc_p$ to $Mc_v$ )
$n$	Exponent in $PV^n$ for polytropic compression, Equation 19
$p$	Absolute partial pressure (in gas mixture), Equation 32
$t$	Temperatures, °C. or °F.
$v$	Partial volume, Equation 33

*Subscripts:*

$P, p$	Constant pressure
$T, t$	Constant temperature
$V, v$	Constant volume

*Greek Letters:*

$\Sigma$	Summation
$\Delta$	Final value — Initial value
$\pi$	Total pressure

## PROBLEMS

The perfect gas laws are to be assumed in the following problems:

1. Show on the  $P$ - $V$  plane the following reversible changes:

(a)  $T = C$ ; (b)  $V = C$ ; (c)  $P = C$ ; (d)  $Q = 0$ ; (e)  $Q = C\Delta T$ .

Make plots of  $\log P$  versus  $\log V$  showing all the above changes.

2. Show on the  $P$ - $V$  plane areas representing the work done, the internal energy change, and the heat added for any reversible process.

3. Show that, if two bodies of the same gas of un-  
tures are mixed adiabatically at constant pressure,

4. Three hundred cubic feet of air in a cylinder at 5 atm. absolute and 90°F. is expanded adiabatically and reversibly to 1 atm. Assuming  $k = 1.40$ , calculate the work done during the change and the final temperature of the gas.

5. Recalculate the preceding problem, assuming the molal heat capacity at constant pressure for oxygen and nitrogen to be  $\overline{Mc}_p = 6.5 + 0.001T$ , where  $T = ^\circ\text{Kelvin}$ .

6. Air at 70°F. and 1 atm. is to be compressed in a turbo-compressor to 3 atm. and then heated to 300°F. The operation of the compressor is essentially adiabatic and reversible. Owing to friction losses the gas at the heater outlet is found to be at only 2.5 atm. pressure. If the apparatus handles 10 mols of gas per minute, what is the smallest motor which can be used to drive the compressor? If the heat be supplied electrically from lines at 440 volts, direct current, what is the minimum amperage the lines must be able to supply?

7. A lagged tank of 100 cu. ft. capacity fitted with a valve contains air at 70°F. and 10 atm. pressure. The valve is opened and the pressure allowed to drop quickly to 50 lb./sq. in. abs. Estimate the final temperature of the air left in the tank.

8. Air originally at 100°C., and 2 atm. is allowed to pass successively through the following series of changes: (1) isothermal expansion to twice its original volume, (2) adiabatic expansion to 20°C., (3) isothermal compression to a condition such that, when (4) adiabatically compressed to 2 atm., it is brought back to its original state. Per mol of air passing through this cycle of changes, calculate (a) the heat added, (b) the net work done, (c) the net change in internal energy.

9. One mol of nitrogen, originally at 2 atm. and 90°F., is expanded polytropically ( $n = 1.2$ ) until its volume has doubled. It is then compressed isopiesticly and next expanded adiabatically until its original volume is attained. On finally compressing isometrically to its original condition it is found that the net work is 0. Calculate for each change the value of  $Q$ ,  $W$ , and  $\Delta E$ .

10. An insulated tank containing  $\frac{1}{10}$  mol of  $\text{N}_2$  at 70°F. and 1 atm. is connected with a second insulated tank of 100 cu. ft. capacity containing methane ( $c_p = 2.48$  joules per gram) at 10 atm. and 100°F. The pressures are allowed to equalize adiabatically. What are the final pressure and temperature?

11. A mixture of methane and steam is being fed to a catalytic reforming unit preceded by a preheater. Steam is supplied dry and saturated at 100 lb./sq. in. abs. while the methane ( $c_p = 2.48$  joules per gram) enters at 500 lb./sq. in. abs. and 90°F. The feed is so adjusted that the molal ratio of gas to steam is 1 to 5. The mixture leaving the preheater is at 850°F. and 20 lb./sq. in. abs.

Calculate, neglecting velocity effects, per 100,000 cu. ft. of mixture leaving the preheater, the B.t.u. added in the preheater.

12. In a portable single-stage compressed-air power unit, air at 70°F. and 1 atm. is compressed to 100 lb./sq. in. gage. Water at a rate of 1 gal./min. is fed to the cooling jackets of the compressor, entering at 50°F., and leaving at 75°F. The air leaves the compressor at 90°F. and passes through a short line to a storage tank of 500 cu. ft. capacity. The temperature of the air in the tank is 75°F. A short air line,  $1\frac{1}{2}$  in. in inside diameter, leads from the tank to a turbine-driven grinding unit exhausting to the atmosphere and rated at 1 hp. The turbine operates essentially adiabatically but with an efficiency of only 50 per cent.

From this information determine, as closely as possible, listing all necessary assumptions:

- (1) The temperature of the air leaving the turbine.

(2) The minimum capacity of the compressor for continuous operation of the turbine under full load.

(3) The minimum power of the motor to run the compressor.

13. A single cylinder air compressor with negligible clearance running at 200 r.p.m. handles 1000 cu. ft./min. of free air at 70°F. Exhaust pressure is 50 lb./sq. in. abs. Calculate the minimum horsepower to drive this machine.

(a) Assuming compression adiabatic.

(b) Assuming compression polytropic,  $n = 1.2$ .

(c) Assuming compression isothermal.

(d) How much heat must be removed during the compression stroke in parts (b) and (c)?

14. A single-stage, single-acting compressor having a clearance equal to 2 per cent of displacement is operating adiabatically and reversibly compressing oxygen from 1 atm. and 70°F. to 4 atm.

(a) What is the work per mol of gas handled?

(b) Assuming displacement is 1 cu. ft., how fast must the machine run to handle 150 cu. ft./min.?

(c) By how much would the work be decreased if compression were polytropic with  $n = 1.2$ , all other steps being the same?

(d) Make a table of capacity per cycle versus clearance for this machine on the assumption that it operates adiabatically throughout. (A suggested range is 1 to 6 per cent.)

15. A single-cylinder, single-acting air compressor having a clearance equal to 3 per cent of displacement is to be used for compressing a hydrocarbon mixture for which  $k = 1.10$ . When compressing air and operating essentially adiabatically and reversibly the machine had a capacity of 500 cu. ft./min. (free air at 60°F.) exhausting into a line where the pressure was 75 lb./sq. in. abs. To what pressure can the same machine compress adiabatically 500 cu. ft./min. (measured at 60°F. and 1 atm.) of the hydrocarbon mixture, the power input to be the same as when air was used? If the compressor operated at 250 r.p.m. on air, at what speed will it operate on the hydrocarbon mixture, and what is the cylinder volume of the machine? Do you anticipate any difficulty when compressing the hydrocarbons, and if so, how would you correct such a difficulty?

16. In a single-stage compressor with adiabatic intake and with compression and expansion following the same law:

(a) How does the work per mol of gas handled vary with the temperature of the gas taken into the cylinder?

(b) How does the work per cycle vary with the intake gas temperature?

(c) What is the effect on the compressor work of cooling during the expulsion stroke?

(d) What is the effect of non-adiabatic intake on compressor work and compressor capacity per cycle?

(e) What effect does change in clearance have on compressor operation?

17. A single-acting, two-stage compressor having a clearance equal to 3 per cent of displacement is handling hydrogen ( $k = 1.42$ ) at 1 atm. abs. and 60°F. Exhaust is at 250 lb./sq. in. abs. With the exception of the intercooler the compressor operates adiabatically.

(a) What must the intermediate pressure be in order that the work may be a minimum?

(b) What assumptions did you make in part (a)?

(c) What is the minimum work necessary per 100 mols of gas handled?

18. Oxygen is flowing through a well-lagged pipe line made up of standard 2-in. iron pipe. The gas enters at 200 lb./sq. in. abs. and 70°F., but owing to friction in the line the outlet pressure is but 20 lb./sq. in. abs. If the gas enters the line with a velocity of 4 ft./sec., at what velocity does it leave?

19. A turbine is to be designed to run on air at 150 lb./sq. in. abs., 70°F. The air will enter a well-designed nozzle at 5 ft./sec., and be expanded down to practically atmospheric pressure. On the assumption that the nozzle operation is adiabatic and reversible but that the overall efficiency of the machine is but 50 per cent of theoretical, estimate as closely as possible:

(a) Condition of the air leaving the turbine.

(b) Mols of air required per horsepower-hour of work done.

20. A long vertical cylinder of negligible heat capacity, open to the atmosphere at one end, fitted with a frictionless piston weighing 50 lb. and having an area of 10 sq. in. contains a mixture of methane and air at 100 lb./sq. in. abs. and 100°F.  $Mc_p$  for the mixture = 8.0. The piston is held in position by a latch. When the latch is released the piston rises, oscillates for some time in the cylinder, and finally comes to rest. The whole apparatus is thoroughly lagged to prevent heat interchange with the surroundings. When the piston finally comes to rest, what is the condition of the gas in the cylinder?

21. A tank of 500 cu. ft. capacity containing air at 2 atm. and 70°F. is to be evacuated to  $\frac{1}{10}$  atm. using a simple single-stage reciprocating pump discharging directly to the atmosphere. Assuming all operations reversible and adiabatic, what expenditure of work will be required to evacuate the tank?

22. Some steel cylinders are to be filled with hydrogen from a constant-pressure line in which the gas is available at 90°F. As the cylinders are shipped they must be under a pressure of 200 lb./sq. in. abs., measured when the cylinders and contents are at 70°F. Assuming the cylinders originally contained hydrogen at 1 atm. and 90°F., what pressure must be held on the line? For hydrogen assume that  $Mc_p = 7.0$ .



## CHAPTER VIII

### GENERALIZED PRESSURE, VOLUME, TEMPERATURE RELATIONS

Many substances, for which pressure-volume-temperature data are incomplete or almost entirely lacking, are of such industrial importance that even an approximate method of estimating their properties would be of distinct aid. Such a condition existed for the hydrocarbons a few years ago. Usually liquid and solid compressibilities, at temperatures considerably removed from the critical, are small, and for materials in these states heat-capacity data at ordinary pressures are often sufficient in engineering calculations. This is not true for gases and vapors, where, in addition to some thermal determinations such as heat capacity, adequate  $P$ - $V$ - $T$  data are necessary.

Despite their known limitations, the gas laws were commonly used in ranges where errors from 5 to 20 per cent were involved, but the recent importance of high-pressure processes, where use of the gas laws may introduce errors in volume of as much as 400 per cent, has made imperative the development of a better calculation technique.<sup>1</sup> Because of lack of data this has for the most part taken the form of approximate relationships. One must not forget that, where dependable data are available, these are to be used, the approximations serving only where such information is lacking.

**$P$ - $V$ - $T$  Approximations for Pure Vapors and Gases.**<sup>2</sup> Inspection of the  $P$ - $V$ - $T$  data for various materials makes apparent the fact that they tend to be similar around the critical. This has resulted in expressing the variables as ratios to the critical values of the material in question, the quantities thus expressed being called *reduced quantities*. If the pressure on a given material is  $P$  and its critical pressure  $P_c$ , its reduced pressure is defined as  $P_R = P/P_c$ . Similarly,  $T_R = T/T_c$  and  $V_R = V/V_c$ . Over fifty years ago van der Waals suggested that the similarity of the  $P$ - $V$ - $T$  curves might be due to the existence of a so-

<sup>1</sup> Thus an error of only 100 per cent in estimating a volume at elevated pressures would introduce not only a similar percentage error in the design of reactors and other expensive equipment, but in addition an error of 300 per cent in the calculation of the kinetic-energy term appearing in many friction computations.

<sup>2</sup> It is assumed throughout this discussion that chemical reaction does not occur.

called reduced equation of state — that by expressing all variables in their reduced form an equation universally applicable would result.

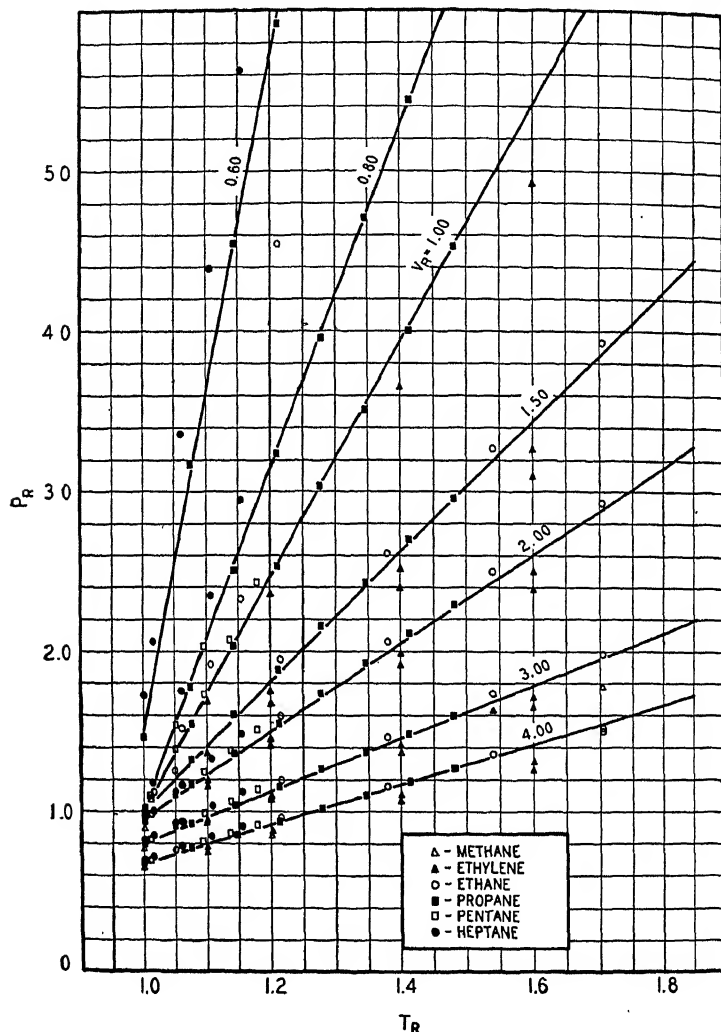


FIG. 1. Reduced Isometrics.

**Reduced Isometrics.** In determining  $P$ - $V$ - $T$  relations, the experimental results are usually obtained in a bomb maintained at constant volume by mechanical compensation. This suggests plotting lines of constant volume, isometrics, on a diagram the ordinate of which is  $P_R$  and the abscissa  $T_R$ . For any chosen material these lines are approx

imately straight. If, instead of volumes on such a plot, lines of constant *reduced* volume are plotted for the various substances, a group of closely grouped lines is obtained at each chosen reduced volume. On Figure 1<sup>1</sup>

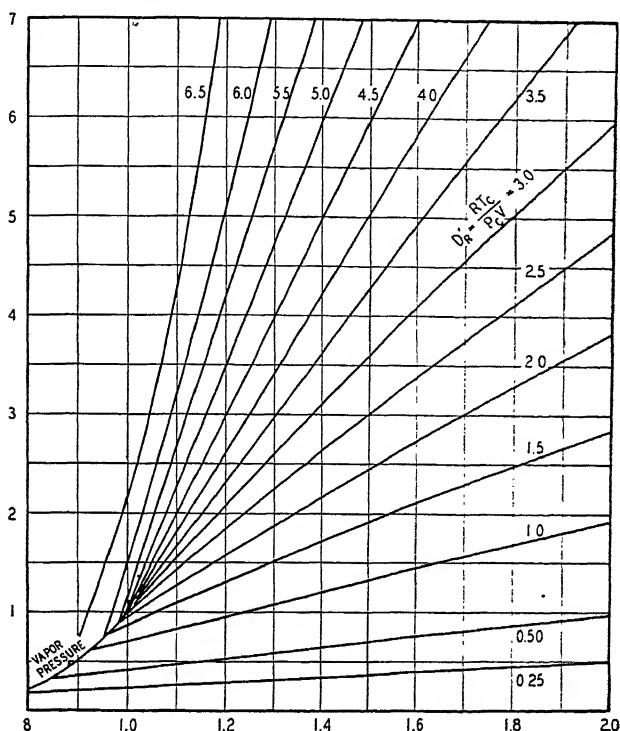


FIG. 2. Pseudo-Reduced Isometrics.

one line in each group has been drawn. Had a universal reduced equation of state existed, each group would have been a single line.

The pseudo-reduced volume is

$$\bar{V}'_R = \frac{V}{V'_c} = \frac{P_c V}{NRT_c} \quad (1)$$

or

$$V = \bar{V}'_R NRT_c$$

In terms of pseudo-reduced density,

$$D'_R = \frac{NRT_c}{P_c V} \quad (2)$$

<sup>1</sup> Data from Kay, Sc.D. Thesis, Mass. Inst. Tech., p. 68, 1937.

By plotting pseudo-reduced volumes a narrower band may be obtained for each group. This will result in a single chart more generally applicable to different groups of substances. At each pseudo-reduced density, Figure 2, based on one mol,<sup>1</sup> has been constructed with a single line representative of all materials.

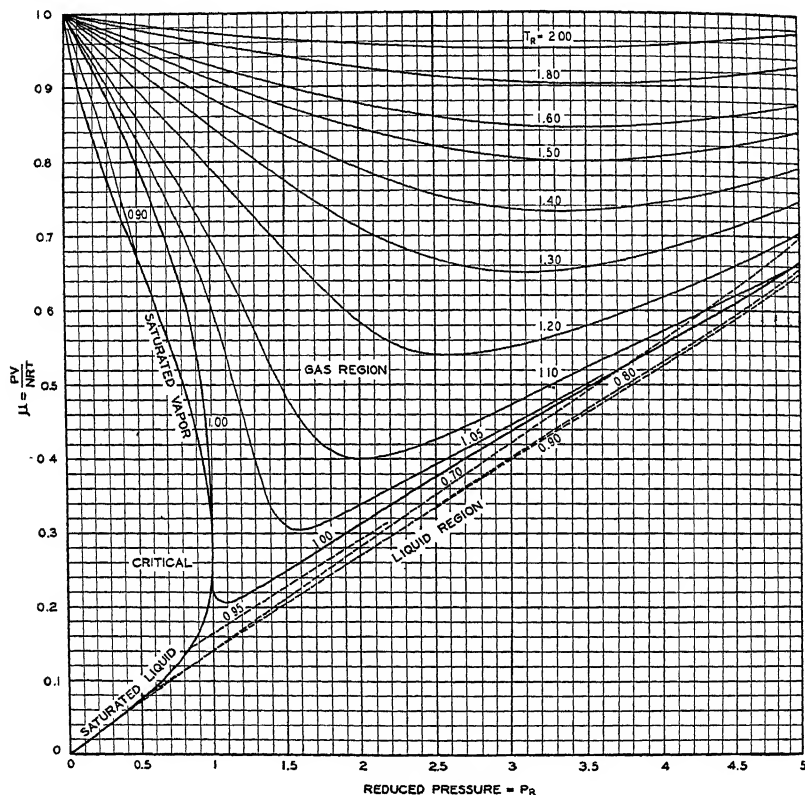


FIG. 3. The  $\mu$ -chart.

**$\mu$ -Charts.** It is difficult to interpolate on Figure 2 for intermediate values of  $V$ . Moreover, isothermal calculations are usually more important industrially than isometric. The isometric plot, Figure 2, is readily transformed to a more convenient form.

The simple gas law expression,  $PV = NRT$ , may be slightly modified by writing

$$PV = \mu NRT \quad (3)$$

where  $\mu$  is merely a correction factor enabling one to use the gas laws

<sup>1</sup> Data for gaseous phase from Su, Sc.D. Thesis, Mass. Inst. Tech., p. 50, 1937.

over any range. For conditions where the gas laws apply,  $\mu = 1$ , and on a molal basis  $\mu$  is always  $PV/RT$ . Note that  $\mu$  is dimensionless and numerically the same in all consistent systems of units.

Figure 3<sup>1</sup> is a plot of  $\mu$  versus  $P_R$  at various values of  $T_R$  for hydrocarbons above methane. Figure 4 is a high-temperature, high-pressure  $\mu$ -chart based on data for hydrogen, oxygen, and nitrogen. Not only do these curves represent the data within their probable accuracy, but in addition the same curves are excellent approximations for most organic compounds and fairly good for all materials except hydrogen and the noble gases or such highly polar compounds as hydrogen cyanide.

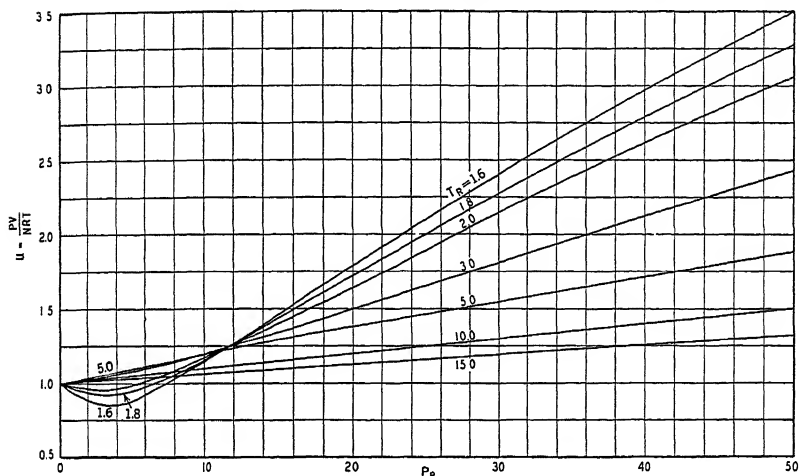


FIG. 4.  $\mu$ -Chart for High Ranges.

To use Figure 3 or 4 only the critical pressure and temperature (Table I) for the material in question are needed. If these are unknown the methods for estimating critical conditions outlined in Chapter VI will be found useful. With the  $\mu$ -charts available, a few or even a single experimental  $P$ - $V$ - $T$  determination may be used to extrapolate over ranges where data are lacking, with a good chance that correct results will be obtained.

**Common Reduced  $P$ - $V$ - $T$  Relations.** It may readily be shown from experimental data that a reduced equation of this form applicable to all materials is impossible. The equation,  $PV = \mu RT$ , for one mol, expressed in reduced form, is

$$\frac{P_R V_R}{T_R} = \mu \frac{RT_c}{P_c V_c} \quad (4)$$

<sup>1</sup> Data for gaseous phase, *ibid.*, pp. 70-84.

TABLE I  
 CRITICAL CONSTANTS\*

Gas	Formula	Molecular Weight	$T_c$		$P_c$ atm.	$\rho_c$ <sup>‡</sup> gm./cc.	$V_c$ liters/mol	$\frac{RT_c}{P_c V_c}$
			°K.	°R.				
Acetic acid	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	60.03	594.8	1070.6	57.2	0.351	0.171	4.99
Acetylene	C <sub>2</sub> H <sub>2</sub>	26.02	309	556	62	0.231	0.113	3.63
Ammonia	NH <sub>3</sub>	17.03	405.56	730.01	111.5	0.235	0.0724	4.12
Argon	A	39.94	151	272	48	0.531	0.0753	3.44
Benzene	C <sub>6</sub> H <sub>6</sub>	78.05	561.7	1011.1	47.7	0.304	0.257	3.76
Butane	C <sub>4</sub> H <sub>10</sub>	58.08	425.17	765.31	37.48	0.2254	0.2576	3.61
Carbon dioxide	CO <sub>2</sub>	44.00	304.26	547.67	73.0	0.460	0.0957	3.58
Carbon monoxide	CO	28.00	132.98	239.36	34.53	0.3010	0.0930	3.40
Carbon tetra- chloride	CCl <sub>4</sub>	153.83	556.3	1001.3	45.0	0.558	0.276	3.69
Chlorine	Cl <sub>2</sub>	70.91	417.2	751.0	76.1	0.573	0.124	3.64
Decane	C <sub>10</sub> H <sub>22</sub>	142.17	619.4	1115	21.24	0.2327	0.611	3.91
Ethane	C <sub>2</sub> H <sub>6</sub>	30.05	305.40	549.72	48.20	0.2032	0.148	3.51
Ethanol	C <sub>2</sub> H <sub>5</sub> OH	46.05	516.2	929.2	63.1	0.275	0.167	4.01
Ethyl chloride	C <sub>2</sub> H <sub>5</sub> Cl	64.50	460.4	828.7	52	0.33	0.196	3.73
Ethyl ether	C <sub>4</sub> H <sub>10</sub> O	74.08	466.0	838.8	35.5	0.263	0.282	3.82
Ethylene	C <sub>2</sub> H <sub>4</sub>	28.03	282.8	509.0	50.9	0.22	0.127	3.58
Helium†	He	4.00	5.26	9.47	2.26	0.0693	0.058	3.28
Heptane	C <sub>7</sub> H <sub>16</sub>	100.12	540.17	972.31	27.00	0.2433	0.411	3.99
Hexane	C <sub>6</sub> H <sub>14</sub>	86.11	507.9	914.3	29.63	0.2344	0.367	3.82
Hydrogen†	H <sub>2</sub>	2.02	33.3	59.9	12.8	0.0310	0.065	3.27
Hydrogen cyanide	HCN	27.02	456.7	822.1	50	0.20	0.135	5.54
Methane	CH <sub>4</sub>	16.03	190.7	343.3	45.8	0.162	0.099	3.46
Methanol	CH <sub>3</sub> OH	32.03	513.2	923.8	98.7	0.272	0.118	4.01
Methyl chloride	CH <sub>3</sub> Cl	50.48	416.3	749.3	65.8	0.37	0.136	3.81
Neon†	Ne	20.18	44.46	80.03	25.9	0.484	0.417	3.37
Nitric oxide	NO	30.01	179	323	65	0.52	0.0578	3.92
Nitrogen	N <sub>2</sub>	28.02	126.1	227.0	33.5	0.3110	0.0900	3.43
Nonane	C <sub>9</sub> H <sub>20</sub>	128.16	596	1072	22.86	0.2319	0.553	3.86
Octane	C <sub>8</sub> H <sub>18</sub>	114.14	569.4	1024.9	24.66	0.2327	0.490	3.85
Oxygen	O <sub>2</sub>	32.00	154.4	277.9	49.7	0.430	0.0744	3.42
Pentane	C <sub>5</sub> H <sub>12</sub>	72.09	470.3	846.6	33.04	0.2323	0.310	3.77
Propane	C <sub>3</sub> H <sub>8</sub>	44.06	369.97	665.95	42.01	0.2260	0.195	3.71
Sulfur dioxide	SO <sub>2</sub>	64.06	430.4	774.7	77.7	0.52	0.123	3.71
Sulfur trioxide	SO <sub>3</sub>	80.06	491.5	884.7	83.6	0.630	0.127	3.80
Toluene	C <sub>7</sub> H <sub>8</sub>	92.06	593.8	1068.8	41.6	0.292	0.315	3.71
Water	H <sub>2</sub> O	18.02	647.30	1165.14	218.53	0.3183	0.05656	4.30

\* Compiled from various sources, especially "International Critical Tables," Vol. 3, pp. 248-249, and Landolt-Börnstein's "Physikalisch-Chemische Tabellen," IIIa, p. 246, 1935.

† For  $P$ - $V$ - $T$  relations, use *pseudo-critical constants*, Table II.

At low pressures  $\mu$  approaches unity. Moreover, for any given substance  $RT_c/P_cV_c$  is fixed, and hence at low pressures  $P_RV_R/T_R$  becomes constant and a function only of  $P$  and  $T$ . However, unless  $RT_c/P_cV_c$  is the same for all substances, this single-valued relation of  $P_RV_R/T_R$  cannot exist, and consequently there cannot be this single reduced equation of state. That the reduced ratio varies for different substances is shown by inspection of Table I, although for certain groups it remains substantially constant. Moreover, this table shows the variation in the critical ratio to be limited. It is therefore possible to formulate an average function in terms of reduced quantities which is a closer approximation to the behavior of most materials than is any other known single relation.

Furthermore, if a common reduced equation of state were possible,  $\mu$  plotted against  $P_R$  for any value of  $T_R$  would yield a single curve applicable to all substances. At a chosen reduced temperature such a plot always does give different lines for the various substances.<sup>1</sup>

**Pseudo-Critical Constants.** Even when the  $\mu$ -curves of Figure 3 or 4 do not adequately fit the experimental values, the two may be made to coincide by using, as critical pressures and temperatures for the substances in question, not the actual ones, but other suitably chosen pseudo-values. Thus Newton<sup>2</sup> suggests that the modified values of  $P_c$  and  $T_c$  given in Table II be used in connection with the  $\mu$ -chart<sup>3</sup> for hydrogen, helium, and neon.

TABLE II  
PSEUDO-CRITICAL CONSTANTS

Gas	$T'_c$ , °K.	$P'_c$ , atm.
Helium .....	8.3	10.3
Hydrogen .....	41.3	20.8
Neon .....	52.5	33.9

# *P-V-T* APPROXIMATIONS FOR GASEOUS MIXTURES

For approximating the *P-V-T* relationships of gas mixtures under conditions where the gas laws are not applicable at least five procedures have been suggested.

1. **Dalton's law of partial pressures** may be assumed valid for the mixture. According to this the *total pressure of the mixture is the sum*

<sup>1</sup> Brown, Souders, and Smith, *Ind. Eng. Chem.*, **24**, 515 (1932); Lewis, *ibid.*, **28**, 259 (1936).

<sup>2</sup> *Ind. Eng. Chem.*, **27**, 302 (1935).

<sup>3</sup> With the  $\mu$ -chart available it is more convenient to use pseudo-critical pressures and temperatures than to revert to the use of pseudo-reduced volumes and the plot of reduced isometrics, Figure 2.

of the pressures of the individual constituents, each measured at the temperatures and total volume of the mixture.

2. **Amagat's law of partial volumes** may be used. According to this the volume of a gas mixture should be the sum of the volumes of the constituents, each measured at the temperature and total pressure of the mixture.

Both these laws are correct where the gas laws apply, but unfortunately both lead to considerable error when dealing with gas mixtures at high pressure.

3. **Kay's method**<sup>1</sup> is much more promising, especially as applied to hydrocarbon mixtures. He assumes that the gaseous mixture can be treated as if it were a pure single-component gas with a pseudo-critical temperature and pressure estimated according to certain rules. The Kay pseudo-critical temperature and pressure for a mixture of known chemical composition are obtained by the following relationships:

$$(T_c)_{\text{mixture}} = (T_c)_a y_a + (T_c)_b y_b + (T_c)_c y_c + \cdots \quad (5)$$

$$(P_c)_{\text{mixture}} = (P_c)_a y_a + (P_c)_b y_b + (P_c)_c y_c + \cdots \quad (6)$$

where

$(T_c)_a$  = critical temperature of pure  $a$ , etc.

$(P_c)_a$  = critical pressure of pure  $a$ , etc.

$y_a$  = mol fraction of  $a$ , etc.

For hydrocarbon mixtures of unknown chemical but known physical characteristics Kay presents a method of estimating pseudo-critical conditions based on the Watson and Nelson<sup>2</sup> characterization factor. The pseudo-critical constants being known, the mixture is handled on the regular  $\mu$ -charts as if it were a single pure component.

4. The **Beattie-Bridgeman equation of state** probably gives more correct values than any of the preceding. For one mol of a gaseous mixture with mol fractions  $y_a$  of pure  $a$ ,  $y_b$  of pure  $b$ , etc., Beattie<sup>3</sup> has proposed weighting the equation constants for the pure components according to the following scheme:

$$A_{0, \text{mixture}} = (y_a \sqrt{A_{0,a}} + y_b \sqrt{A_{0,b}} + y_c \sqrt{A_{0,c}} + \cdots)^2$$

$$a_{\text{mixture}} = y_a a_a + y_b a_b + y_c a_c + \cdots$$

$$B_{0, \text{mixture}} = y_a B_{0,a} + y_b B_{0,b} + y_c B_{0,c} + \cdots$$

$$b_{\text{mixture}} = y_a b_a + y_b b_b + y_c b_c + \cdots$$

$$C_{\text{mixture}} = y_a c_a + y_b c_b + \cdots$$

<sup>1</sup> *Ind. Eng. Chem.*, **28**, 1014 (1936).

<sup>2</sup> *Ind. Eng. Chem.*, **25**, 880 (1935).

<sup>3</sup> *J. Am. Chem. Soc.*, **51**, 19-30 (1929).



The equation of state for the mixture is:

$$P = \frac{RT(1-e)}{V^2} (V+B) - \frac{A}{V^2} \quad (8)$$

where

$$A = A_{0, \text{mixture}} (1 - a_{\text{mixture}} / V).$$

$$B = B_{0, \text{mixture}} (1 - b_{\text{mixture}} / V).$$

$$e = c_{\text{mixture}}$$

If the Beattie-Bridgeman constants are known, this method gives satisfactory results at volumes greater than the critical.

5. **Gilliland's method**<sup>1</sup> is a modification of the procedure previously suggested using the Beattie-Bridgeman equation of state, but with the simplifying assumption that for most mixtures the constant volume or isometric curves plotted on the  $P$ - $T$  plane are straight lines.

The principles may be briefly outlined. For a pure component assuming the isometrics straight, Figure 5, the relation between pressure and temperature is:

$$P = \phi_1 T - \phi_2 \quad (9)$$

where  $\phi_1$  is the slope and  $\phi_2$  is the intercept at  $T = 0$ .

Values of  $\phi_2$  for various materials have been correlated by plotting  $(\phi_2)_R = \phi_2/P_c$  against  $V_R = V/V_c$  as in Figure 6. For the mixture

$$P_{\text{mixture}} = (\phi_1)_{\text{mixture}} T - (\phi_2)_{\text{mixture}} \quad (10)$$

$$\text{where } (\phi_1)_{\text{mixture}} = y_a(\phi_1)_a + \quad (11)$$

It will be noted that the slopes  $(\phi_1)_a$ ,  $(\phi_1)_b$ , etc., are evaluated at the same temperature and same molal concentration as the mixture itself. The intercept  $(\phi_2)_{\text{mixture}}$  is evaluated according to the empirical relation.

$$(\phi_2)_{\text{mixture}} = [y_a \sqrt{(\phi_2)_a} + y_b \sqrt{(\phi_2)_b} + y_c \sqrt{(\phi_2)_c} + \dots]^2 \quad (12)$$

Figure 6 may be used to estimate  $\phi_2$ , etc., the intercepts, for the constituents of the mixture.

<sup>1</sup> *Ind. Eng. Chem.*, **28**, 212 (1936).

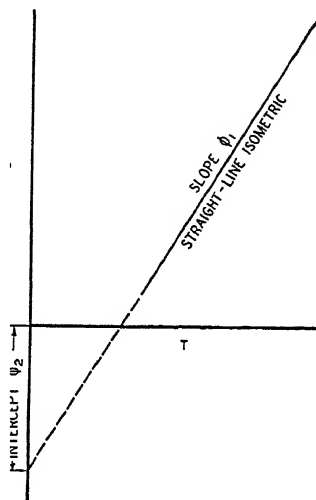


FIG. 5. Extrapolation of Straight-Line Isometric.

Given the slopes and intercepts for the isometrics of the mixture, its isometrics may be constructed on the  $P$ - $T$  plane. From a series of these the complete  $P$ - $V$ - $T$  relations for the mixture may be estimated.

With the limited data available in the literature it is difficult to say which of the preceding methods is preferable. None is strictly dependable in the critical region.

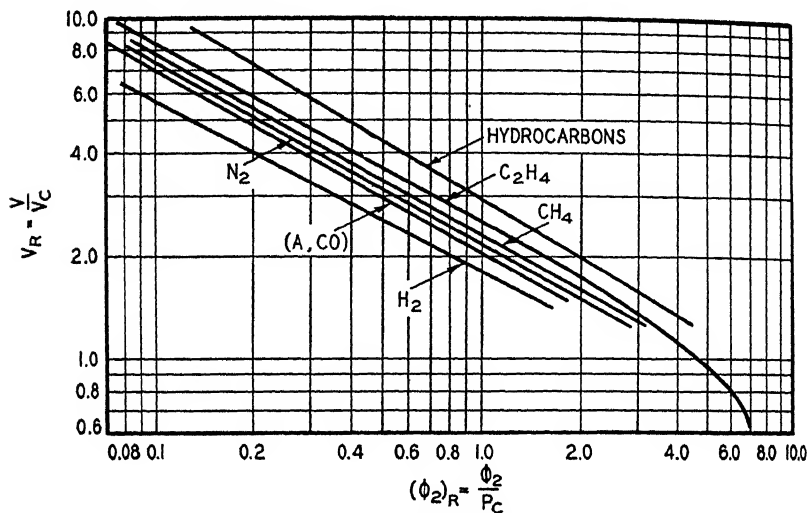


FIG. 6. Plot for Obtaining Values of  $\phi_2$ .

#### $P$ - $V$ - $T$ RELATIONS FOR PURE LIQUIDS

On a basis of  $\mu$ , the  $P$ - $V$ - $T$  relations for a few pure liquids have been correlated<sup>1</sup> and are presented on Figure 3. The results are based on somewhat limited work and consequently are to be considered only as tentative. However, where good experimental results are lacking this correlation is recommended.

#### NOTATION FOR CHAPTER VIII

##### *Upper Case:*

$A, A_0$	Constants in the Beattie-Bridgeman equation
$B, B_0$	Constants in the Beattie-Bridgeman equation
$D$	Molal density, mols/liter or mols/cubic foot
$D'_R$	Pseudo-reduced density, $NRT_c/P_c V$
$N$	Number of mols
$R$	Gas constant
$T$	Absolute temperature, °K., °R.

<sup>1</sup> York, private communication, July, 1938.

$V$	Volume
$V_R$	Reduced volume, $V/V_c$
$V'_R$	Pseudo-reduced volume, $P_c V'/NRT_c$

*Lower Case:*

$a, b, c, e$	Constants in the Beattie-Bridgeman equation
$y$	Mol fraction in gaseous phase

*Subscripts:*

$R$	Reduced quantity, value/value at critical
$c$	Critical state
$a, b, c$	Component, $a, b, c$ , etc.

*Greek Letters:*

$\rho$	Density, gm./cc., lb./cu. ft.
$\mu$	Compressibility factor, $PV'/NRT$
$\phi_1$	Slope of isometric
$\phi_2$	Intercept of isometric at $T = 0$

## PROBLEMS

1. Using steam-table data, construct on a plot of  $\mu$  versus  $P_R$ , the isothermal  $T_R = 1.20$ , and compare it with the same isothermal drawn on the  $\mu$ -charts. Why is the agreement not closer?

2. Using the  $\mu$ -charts, calculate the specific volume of steam at:

- (a) 3400 lb./sq. in. and 800°F.
- (b) 3226 lb./sq. in. and 706.1°F.

Compare your results with those given by the steam tables and with those obtained by assuming the gas laws.

3. Calculate the work of compressing 1 mol of ethylene reversibly from a pressure of 748.5 lb./sq. in. to 2244 lb./sq. in. at a constant temperature of 535°R.:

- (a) In a non-flow process.
- (b) In a flow process.

4. Methane originally at 1 atm. and  $-40^\circ\text{C}$ . is to be compressed isothermally in a rotary compressor to 130 atm. Per mol of gas handled, what is the minimum work required?

5. How do you explain the fact that the lines of reduced temperature cross each other in some ranges of the  $\mu$ -charts?

6. For ethylene construct with the aid of the  $\mu$ -charts isometric lines on the  $P_R$  versus  $T_R$  plane at values of  $V_R = 0.80$  and 1.20.

7. An oxygen cylinder originally under a pressure of 2000 lb./sq. in. abs. at  $20^\circ\text{C}$ . is now found to be at a pressure of 250 lb./sq. in., the temperature of the cylinder and contents still being at  $20^\circ\text{C}$ . What volume fraction measured (at  $20^\circ\text{C}$ . and 1 atm.) of the original contents still remains in the cylinder?

8. Using data from the steam tables, estimate the volume occupied by 1 lb. of  $\text{SO}_2$  vapor at 110 lb./sq. in. abs. and  $130^\circ\text{F}$ .

9. Masson and Dolley (*Proc. Roy. Soc.*, 103A, 524 [1923]) obtained the following experimental data on a gaseous mixture of ethylene and argon at 25°C.

Mol per cent ethylene	= 59.86%
Mol per cent argon	= 40.14%
Pressure	= 120 atm.
Volume	= 0.1388 liter/mol

Using the  $\mu$ -charts for  $P$ - $V$ - $T$  relations, calculate the pressure or volume of this mixture by each of the following methods:

- (a) Dalton's law.
- (b) Amagat's law.
- (c) Kay's method.
- (d) Gilliland's method.

## CHAPTER IX

### THE SECOND LAW OF THERMODYNAMICS

The second law is merely a statement of the results of many experiments. To derive a quantitative mathematical expression, the perfect gas laws will be assumed for the system, but the results obtained will not be limited by this assumption. For simplicity and clarity, discussion will first be restricted to *reversible cyclical processes* made up of two isothermals and two adiabatics. This will be broadened by successively showing how:

- (a) The process may be *any cyclical reversible process*.
- (b) The process may be *any reversible process*.
- (c) The process may be *any process whatsoever*.

Finally, really as a corollary to the previous discussion, it will be shown that the experimentally determined perfect gas temperature scale actually is the same as one of the many possible fundamental, thermodynamic temperature scales.

Although for two centuries heat has been used on an ever-increasing industrial scale as a source of mechanical work, it has been the universal experience that efficiency of conversion from heat to work is always low. Most modern steam power plants have an efficiency of not more than 25-30 per cent, and in even the best internal-combustion engines an efficiency of over 40 per cent is seldom realized. This is in sharp contrast to the well-recognized fact, already emphasized, that work is always quantitatively and completely convertible to heat.

In such a situation one is inclined to explain the low efficiency of the mechanism employed for converting heat to work by assuming incorrect design or practical difficulties in construction. But so low were the efficiencies always found, and so fruitless all efforts at markedly increasing them, that it was finally inferred that these low efficiencies were due to some fundamental underlying natural limitation governing the convertibility of heat to work. This impossibility of completely converting heat to work was first recognized by Sadi Carnot (1796-1832), one of the outstanding workers of all time in thermodynamics.

In the history of human endeavor negative statements are usually not broadly constructive. Generally, their major utility is the elimination of faults and the clearing of ground for germination and growth of new ideas. This particular negation, however, has proved an exception in

that, when coupled with well-known and recognized facts, it has become a positive aid in understanding the nature of heat.

### GENERAL STATEMENT OF THE SECOND LAW PRINCIPLE

The fundamental principle underlying the second law has been expressed in many ways, all of which are quantitatively equivalent. Choice for the form of expression is therefore arbitrary. In this discussion the following will be employed as an initial statement of the principle.

**Any process, the sole net result of which is equivalent to the transfer of heat from a low temperature level to a high one, is impossible.**

This is sometimes stated less elegantly but perhaps more simply by saying, "Heat will not of its own accord flow uphill."

Like the first law, the second rests on experimental evidence without which no amount of mathematical manipulation or reasoning can lead to the result here stated. Until tried it could not be predicted that, when two bodies at unequal temperatures are placed in contact, the hotter will become colder, and the colder, hotter. Never, in the almost countless number of times this experiment has been repeated, has any contradiction been detected. Many were reluctant to admit the truth of the fundamental facts. As a result all sorts of arrangements have been suggested in attempts to devise an apparatus to circumvent the second law. All have failed. Of late years, partly because of the overwhelming experimental evidence and partly because of a more complete and general understanding of the concepts, the engineer has clearly realized the hopelessness of finding an exception to this fundamental law.

The second law statement is restricted to changes in which the sole net result is a transfer of heat. This requires that there be no other net change in the system or in any part of the surrounding universe. As for the system, absence of other changes in it can be assured only if the process is cyclical in nature, that is, so operated that conditions in the system after all changes have occurred are identical with those at the beginning. The statement is limited to transfer of heat from one temperature level to another. Since in a cyclical process there can be no *net* change within the system itself, the exchange of heat referred to must be between the system and its surroundings. Consequently, in the form stated the second law principle is applicable only to a process cyclical from the point of view of the system under consideration and so carried out that changes in the surroundings are limited to :  
**of heat from one temperature level to another.**

In the pages to follow, many important and sometimes involved deductions will be made from the simple, easily demonstrated second law statement. It will be helpful for the beginner to reread this section as the argument develops.

**Heat Engines.** Any mechanism the primary purpose of which is the conversion of heat to work is a **heat engine**. Examples are found in the steam engine and steam turbine power plant (Figure 1), the various types of internal-combustion engines, and many of the now obsolete hot-air engines (Figure 2). In a heat engine the working substance is the material, physical changes in which render possible absorption of

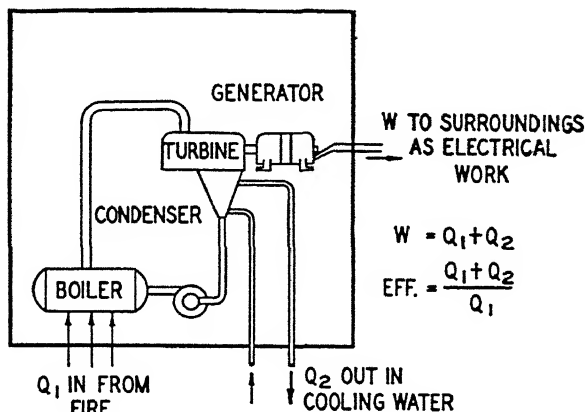


FIG. 1. Steam Power Plant as a Heat Engine.

heat and its conversion, in part at least, to work. In a cyclical heat engine the working substance remains within the mechanism, unchanged in quantity, and periodically returns to its initial state. For example, a steam power plant wherein water is evaporated in a boiler, passed through an engine or turbine, condensed, and returned to the boiler is a cyclical heat engine. The "heat engine" is the combination of boiler, engine, and condenser together with auxiliary apparatus—not the engine alone. In a *reversible cyclical heat engine* not only does the working substance undergo a cycle of operations but in addition each change is thermodynamically reversible.

**Quantitative Formulation of the Second Law.** Despite its negative character, it is possible to give the second law principle positive quantitative formulation. This will be done by means of the following analytical steps:

1. It is a fact that work can be produced from heat by means of a heat engine. Actually cyclical engines, by careful design and

operation, can be made to approximate reversibility and almost always can be conceived as reversible for purposes of logical analysis.

2. Any cyclical heat engine must absorb heat from its surroundings and give up the generated work to its surroundings; otherwise, its operation would involve a violation of the law of energy conservation. In addition, experiment shows that every operative cyclical heat engine

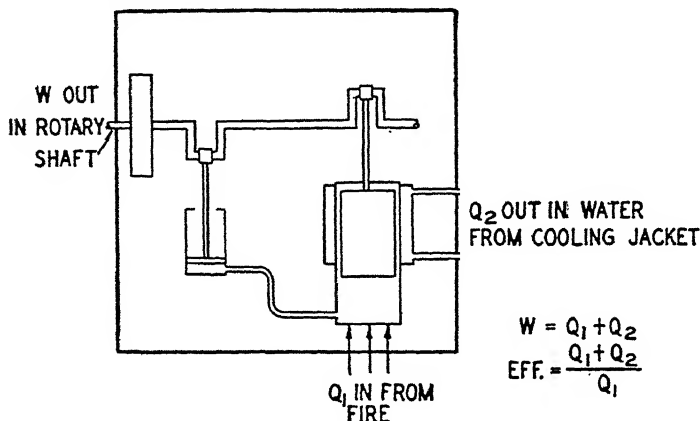


FIG. 2. Diagram of Hot Air Engine.

#### CYCLE OF OPERATIONS

Air held in the larger cylinder is heated by energy coming in from the burning fuel. The air expands and in so doing pushes the piston in the smaller cylinder to the top of its stroke. By the crank arrangement shown this movement pushes the transfer piston, a loosely fitting mass in the larger cylinder, to the bottom of its travel. This causes the heated air to flow between the transfer piston and its cylinder walls to the upper water-cooled end of the cylinder. Here cooling of the gas against the cold cylinder walls causes a pressure drop, whereupon the atmosphere, pushing on the smaller power piston, forces it once more to the bottom, the transfer piston simultaneously moving to the top of its stroke. This completes the cycle and the apparatus is once more ready to repeat the series of changes for the next revolution of the engine shaft. Such engines easily run several hundred revolutions per minute and although they are fairly efficient yet, because of their size and weight for a given power output, they are almost never seen today. It is interesting to note that the working substance, the gas, never leaves the engine but is merely transferred back and forth between the two cylinders.

not only absorbs heat but also gives up some heat to its surroundings. The heat is rejected at lower temperature levels than those at which it was absorbed.

3. For simplicity it is preferable to consider first cyclical heat engines whose operation is restricted to absorbing heat at a *fixed high temperature* level, and rejecting heat at a *second fixed low temperature* level. This is equivalent to assuming all operations involving heat exchange with the surroundings isothermal and all other changes adiabatic. For the time being, discussion will be limited to engines of this specific type.

4. An irreversible cyclical heat engine does not have the same efficiency as a reversible one, both working between the same two



ture levels, *i.e.*, taking in all heat at a single temperature  $t_1$  and rejecting all heat at a single temperature  $t_2$ . But no cyclical heat engine can be more efficient than a reversible one, provided that both operate between the same two temperature levels.

If this were not true the more efficient non-reversible engine could be used to run the reversible. This would result in pumping the heat rejected by the reversible uphill and having left over some work with which to pump additional heat. The *sole net result* accomplished by such an operation would be the transfer of heat from a low temperature level to a high. Therefore, the irreversible engine must be less efficient than the reversible.

5. All reversible cyclical heat engines operating between the same two temperature levels must have the same efficiency. To prove this, assume any two such engines, both operating between the two temperature levels,  $t_1$  and  $t_2$ , heat exchange with the surroundings always being limited to these temperatures. The first of these engines absorbs a quantity of heat  $Q_1$  at the high temperature  $t_1$ , operates through its cycle, and converts into work a certain fraction,  $e$ , of the heat absorbed at the higher level. The remainder of the absorbed heat  $Q_2$  is rejected at the temperature level  $t_2$ . Assume a second engine operating between the same temperature limits, but capable of converting to work a fraction  $e'$  (of  $Q_1$ ) numerically less than  $e$ . Let this engine be operated in a direction thermally opposite to the first, *i.e.*, absorbing heat at  $t_2$  and rejecting it at  $t_1$ . Operate and proportion this second engine so that the work it *consumes* in a given single cycle is exactly equal to the work *performed* by the first engine in a single cycle. Since its efficiency is lower than that of the first, it will absorb more heat at the lower temperature level than the first rejected and reject more heat at the higher temperature level than the first absorbed. The total result of operating these two engines is equivalent to absorbing a net quantity of heat at the low temperature level  $t_2$  and transferring it to the high temperature level  $t_1$ . Experiment teaches that this is impossible. Lacking adequate reason to question the soundness of the logic, one must conclude that an assumption of differences in efficiencies between the two reversible heat engines is erroneous. In short, any two reversible cyclical heat engines operating between the same two temperature levels must have the same efficiency, irrespective of (a) the nature of the working substance, (b) the character of the process.

6. Because the efficiency of converting heat to work is the same in all reversible cyclical heat engines operating between the same two temperature levels, this efficiency may be calculated by employing any working substance for which data are available. Abundant data are at hand

for the monatomic perfect gases. In addition, since for these  $C_v$  is constant, the mathematics is elementary. *The results to be obtained using a perfect monatomic gas as a working substance are general and in no way limited by the characteristics of such gases.*

**Derivation of a Mathematical Second Law Expression.** Figure 3 represents, on the  $P$ - $V$  plane, operation of a reversible cyclical engine using a monatomic perfect gas as a working substance.

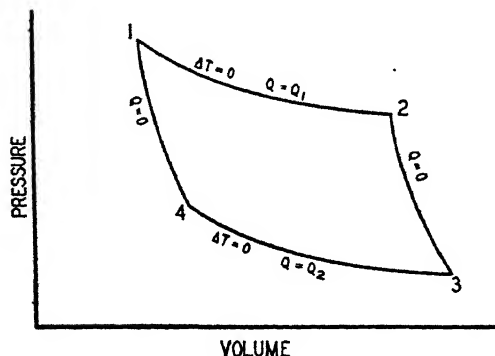


FIG. 3. Pressure-Volume Relations for the Carnot Cycle.

Process 1-2 is an isothermal reversible expansion at  $T_1$  during which a quantity of heat  $Q_1$  is absorbed while 2-3 is an adiabatic reversible expansion to  $T_2$ . Process 3-4 is an isothermal reversible compression at  $T_2$  during which a quantity of heat  $Q_2$  is rejected and 4-1 represents an adiabatic reversible

compression of the gas from  $T_2$  to  $T_1$ , its original condition. After its proposer, Sadi Carnot, this is known as a **Carnot cycle**. Tabulating all heat and work effects along the four processes and basing the calculations on one mol of gas:

Process	Heat Absorbed by the Gas (Withdrawn from the surroundings)	Work Done by the Gas
1-2	$RT_1 \ln \frac{P_1}{P_2} = Q_1$	$RT_1 \ln \frac{P_1}{P_2}$
2-3	0	$-C_v(T_2 - T_1)$
3-4	$-RT_2 \ln \frac{P_4}{P_3} = Q_2$	$-RT_2 \ln \frac{P_4}{P_3}$
4-1	0	$+C_v(T_2 - T_1)$

By algebraic manipulation,

$$\frac{P_1}{P_2} = \frac{P_4}{P_3}$$

This may also be shown graphically by plotting the Carnot cycle using scales of  $\log P$  versus  $\log V$ .

The efficiency is therefore<sup>1</sup>

$$\frac{W}{Q_1} = \frac{Q_1}{Q_1} - \frac{Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} \quad (1)$$

This equation is derived on the implied assumption of a finite difference in temperature between the temperature levels,  $T_2$  and  $T_1$ . However, the equation is independent of the magnitude of this difference. If derived for differential differences,  $T_1 = T_2 + dT$ . Under these conditions the work recovered would be a differential quantity,  $dW$ , despite the fact that a finite quantity of heat,  $Q_1$ , is absorbed at the higher temperature level. In other words,

$$\frac{dW}{Q_1} = \frac{dT}{T_1} \quad (2)$$

In such an equation the quantities  $Q_1 + Q_2$  and  $T_1 - T_2$  are differential only and therefore negligible in comparison with the terms  $Q_1$  and  $T_1$ . The subscripts can be dropped and a new equation written

$$\frac{dW}{Q} = \frac{dT}{T} \quad (3)$$

By algebraic rearrangement Equation 1 may be written

$$\frac{Q_2}{T_2} = -\frac{Q_1}{T_1}$$

or

$$\frac{Q_2}{T_2} + \frac{Q_1}{T_1} = 0 \quad (4)$$

These quantitative relations were derived on the assumption that the working substance was a perfect monatomic gas, but, as already pointed out, the equations must be universally valid for the conditions for which they were derived, irrespective of the working substance.

Summarizing: For any cyclical, reversible process, in which there is no interchange between the system and the surroundings other than work and heat, the heat being exchanged at two constant temperature levels only, all other changes being adiabatic, the relation between the work and heat effects is

$$\frac{W}{Q_1} = \frac{T_1 - T_2}{T_1}$$

<sup>1</sup> It may appear unusual to see the plus sign connecting the two heat quantities, but it must be remembered that  $Q_2$  is inherently negative.

If  $T_1 - T_2$  is differential, this becomes

$$\frac{dW}{Q} = \frac{dT}{T}$$

In every such process the algebraic sum of all the heat absorbed divided by the temperature at which it is absorbed is zero, *i.e.*,

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

**Generalized Characteristics of Reversible Cyclical Processes.** The equations just derived are impressive in their implications. None the less they are rigidly limited by the requirements:

1. That operation be cyclical and reversible.
2. That heat transfer be isothermal and at two definite temperature levels.

To expand greatly the generality of these relations is relatively easy. Consider any reversible cyclical process using any working system,

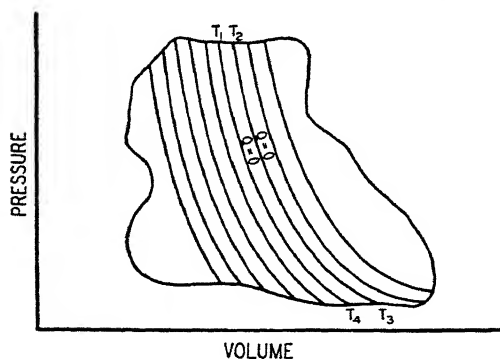


FIG. 4.

however complicated. It may be helpful to conceive the process represented diagrammatically as in Figure 4. The axes are pressure and volume, but any suitable parameters may be employed. Since the process is cyclical it must be represented by a closed diagram, but since it is not restricted in its general nature the diagram is likely

to be of any irregular shape. On this diagram draw an infinite number of curves representing reversible adiabatic changes, adjacent curves separated at each point by differential values of the parameters employed, in this case pressure and volume. These differential values are chosen sufficiently small that any change in temperature occurring along the outer curves, representing the original cycle, is, between two adjacent adiabats, a differential of order higher than the first. This results in dividing the original diagram into an infinite number of diagrams, each representing a complete cyclical reversible process with two legs adiabatic and the other two isothermal. Consequently each of these differential cyclical reversible processes conforms to the limitations under which Equations

tions 1-4 were derived. Since, however, the isothermal legs of the differential cycles represent but a differential change, the heat absorbed or rejected along them must be a differential quantity,  $dQ$ . But, for any of these cycles,  $dQ_1/T_1 + dQ_2/T_2 = 0$ .

The two isothermal legs of each differential cycle are differential sections of the curve representing the original cycle. Furthermore, the differential isothermal legs appear only once in the general cycle and are never duplicated. Finally, the total path of the original cycle is the sum of these differential elements. The sum of the differential isothermal heat effects,  $dQ_1$ ,  $dQ_2$ , etc., is the heat effect for the general cycle. Since the differential processes are cyclical, there can be no internal energy changes within the system itself. Consequently, the algebraic sum of these differential heat quantities for the *cycle as a whole* must equal the total work done by the cycle, i.e.,  $\int dW = \int dQ$ . Turning attention to the terms  $dQ_1/T_1$ ,  $dQ_2/T_2$ , etc., it is obvious that for every  $dQ/T$  on the high-temperature side there must be a corresponding  $dQ/T$  on the low-temperature side, counterbalancing the first and making the algebraic sum of the two zero. This is true for every element of the whole cycle. Therefore it must be true for the complete cycle itself.

These relations are summarized in the following statement: **For any cyclical reversible process, the algebraic sum of the heats added to the system, divided by the temperatures at which they are added, must be zero.** Mathematically,  $\int dQ/T$ , taken around the complete cycle, is zero.

#### Generalized Characteristics of Reversible Processes.

Let the full curve of Figure 5 represent any cyclical process. Starting at *A*, follow the path of this process to point *B*. Along this path  $\int dQ_{\text{rev.}}/T$  will not

in general be zero. For example, over the whole of the path the system may have been receiving heat from its surroundings and as a result  $\int dQ_{\text{rev.}}/T$  is a positive, finite quantity. Now complete the cycle by proceeding around the diagram in the same direction along the full curve back to *A*. From *A* back to *A*,  $\int dQ_{\text{rev.}}/T$  must be zero. Therefore

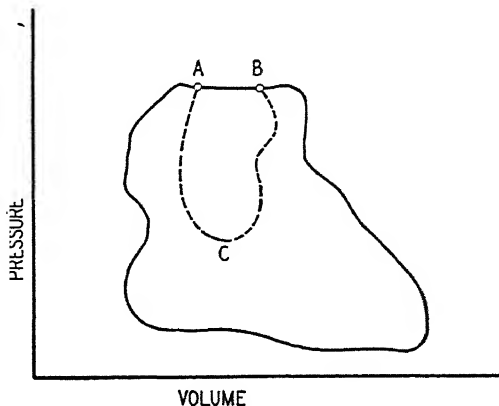


FIG. 5.

the value of this integral between  $B$  and  $A$  on the second part of the cycle must be numerically equal and opposite in sign to the value of the corresponding integral in going from  $A$  to  $B$ .

Let the dotted curve of Figure 5 represent any other reversible path between  $B$  and  $A$ . The process represented by the full curve from  $A$  to  $B$  in combination with the dotted curve from  $B$  back to  $A$  also corresponds to a cyclical reversible process. Consequently,  $\int dQ_{\text{rev.}}/T$  over this cycle,  $A-B-C-A$ , must likewise be zero. However, the value of this integral from  $A$  to  $B$  on the second cycle is obviously identical with its value on the first discussed. Therefore,  $\int dQ_{\text{rev.}}/T$  from  $B$  back to  $A$  must be the same along both full and dotted curves. The sole limitation for these two curves was that each represents a reversible path from  $B$  to  $A$ . It follows that  $\int dQ_{\text{rev.}}/T$  between any two definite states of a system must be the same along all reversible paths.

Mathematically, this is equivalent to saying that for all processes the quantity  $\int dQ_{\text{rev.}}/T$  is a point function independent of the path *whether reversible or not*. However, *the function can be evaluated by integration only along some known reversible path or its equivalent*.

As it was desirable to call  $E + PV$  the enthalpy, so it is convenient to call the function

$$\int \frac{dQ_{\text{rev.}}}{T}$$

*change in entropy*.

$$S_A - S_B = \Delta S_{B \rightarrow A} = \int_B^A dQ_{\text{rev.}}$$

It must be evident that along any *reversible isothermal*

$$\Delta S = \frac{Q_{\text{rev.}}}{T}$$

and along any *reversible adiabatic*,

$$\Delta S = 0$$

**Perpetual Motions.** A fundamental difference exists between the underlying concepts of the first and second laws. The first affirms the impossibility of creating or destroying energy. The second, presupposing the first, affirms that the transformation of heat to work *is limited quantitatively by the temperature level of the heat*, in accordance with the second law equation. Both express limitations to our possibilities of achievement.

So important is energy that new sources are always being sought. According to the first law these sources cannot in fact be new but are limited to reservoirs of energy already existing. In the *practical* utilization it is necessary first to convert the stored energy to heat and from this evolve other forms of energy, *i.e.*, work. According to the second law this conversion of heat to other forms cannot be complete but is limited in efficiency. In an effort to fulfill our energy requirements the investigator and more particularly the inventor is prone to make the futile attempt either to create energy or to exceed the possibilities of converting heat energy into other forms. The two fundamental laws of thermodynamics state that in either event he is doomed to failure. Any machine or process proposed to transcend either of these laws is called a *perpetuum mobile*. However, the two impossibilities are so different in kind that different names are used for the various devices proposed to avoid these limitations. A device to circumvent the first law is called a *perpetuum mobile* of the first order; the second, a *perpetuum mobile* of the second order.

#### LIMITATIONS OF THE SECOND LAW

The underlying cause for the limitation in converting heat to work has been the subject of far-reaching analysis. Perhaps the first clear insight into the nature of the problem other than mathematical came from Maxwell.

An insulated box filled with any gas and having a partition separating the box completely into two sections is assumed. In the partition is a tiny frictionless gate controlled by an intelligent being or "demon" capable of observing molecular motion, a Maxwell Demon. He watches, and whenever a fast-moving gas molecule, one of higher than the original average gas temperature, approaches the gate on the left side he allows it to pass through to the right. Similarly he allows slow-moving molecules to pass to the left side. This causes a rise in temperature of the gas in the right side of the box and a fall in that on the left. Disregarding the demon, this will be the sole net result. Such a system circumvents the second law, but not the first.

Boltzmann suggested another technique which avoids any necessity for intelligence in the actual operation of the process. Assume a cell containing an extremely dilute solution of colloidal iron. Place this between the poles of a permanent magnet having poles of dimensions approximating those of the iron particles. The magnet is provided with a coil from which a current developed by the Brownian movement of the iron particles past the magnet poles can be drawn. To maintain the colloidal motion (hold the temperature constant) the whole may be immersed in the ocean, which serves as a reservoir from which to draw heat energy. The sole net result of operating this system would be the

conversion of a quantity of heat to work — an impossible result according to the second law.

In all such cases we are either enlisting the aid of conscious choice to differentiate between particles of molecular dimensions or dealing with a number of particles so limited that the law of probability does not hold.

The second law applies to those processes where the number of molecules involved is large enough and the conditions such that the law of probability is applicable. This leads to an interesting connection between entropy and probability, a discussion beyond the scope of this book.

Actually the second law applies to every case of practical importance where heat is converted to work.

### THERMODYNAMIC TEMPERATURE SCALE

Consideration of the second law expression indicates that it contains certain fundamental elements and others superficial and arbitrary. Thus, temperature is evidently a fundamental property of matter, but the scale in which it is expressed is arbitrary. However, the relation between the *thermodynamic efficiency* of the reversible cyclical heat engine, operating between two definite temperature levels, and the *temperature* is clearly fundamental in nature. Because the choice of temperature scale was optional the particular equation which has been derived representing this relation contains this inherent arbitrariness.

It is possible, however, to segregate the fundamental from the arbitrary. It may be said that a necessary functional relation exists between the convertibility of heat to work and the temperature level of the heat. This relation must be independent of the units in which either energy or temperature is expressed. Since nothing is gained by choosing a complicated relation, assume

$$\frac{Q_1 + Q_2}{Q_1} = \frac{\theta_1 - \theta_2}{\theta_1}$$

where  $Q_1$  = heat absorbed at  $\theta_1$  and  $Q_2$  = heat absorbed at  $\theta_2$ . This is a reasonable assumption and is in agreement with the similar relation developed by using a perfect monatomic gas as a working substance, namely,

$$\frac{Q_1 + Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$$

Evidently  $T$  is proportional to  $\theta$ , and for simplicity they are made the same. Thus the thermodynamic temperature scale corresponds to the absolute scale experimentally determined with the aid of a gas thermometer.



## SUMMARY

1. Any process the sole net result of which is equivalent to the transfer of heat from a low temperature level to a high is impossible.

2. For any cyclical reversible process wherein a quantity of heat is absorbed at a single temperature  $T_1$ , and a part of this is rejected at a second single temperature  $T_2$ , the fraction converted to work is

$$\frac{W}{Q_1} = \frac{T_1 - T_2}{T_1}$$

or for a differential process

$$\frac{dW}{Q} = \frac{dT}{T}$$

3. For any reversible cyclical process

$$\int \frac{dQ_{\text{rev.}}}{T} = 0$$

4. For any process  $\frac{\lambda_{\text{rev.}}}{T}$  is independent of the path, provided that a reversible path is chosen along which to evaluate the integral. This important function is called the entropy. Change in entropy =  $\Delta S = \int_{\text{Initial}}^{\text{Final}} \frac{dQ_{\text{rev.}}}{T}$ .

5. The experimentally determined perfect gas temperature scale coincides with the fundamental thermodynamic temperature scale.

## PROBLEMS

1. Derive the Clapeyron equation in its exact and approximate forms.

*Solution.* One interesting derivation of this important relation based on the second law is as follows:

Let  $A-B$  represent a reversible monovariant change at pressure  $P$  such as an evaporation, fusion, a chemical reaction, or a change in crystal form. The heat absorbed at  $T$  during this change is  $Q$ . At condition  $B$  let the pressure be changed to  $P - dP$ , the temperature changing to  $T - dT$ . Now allow a monovariant change the opposite of that from  $A$  to  $B$ , to bring the system to state  $D$ . During this change heat will be rejected. Finally increase the pressure by  $dP$  (and the temperature by  $dT$ ), restoring the system to its original condition at  $A$ .

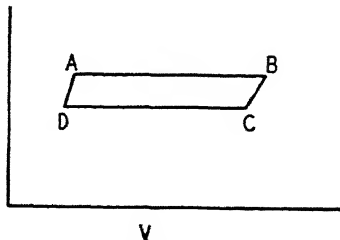


FIG. 6.

The heat effects between  $B-C$  and  $D-A$  are differential in magnitude. Moreover, any volume changes resulting from the differential changes in pressure mentioned are also differential and negligible in comparison with the finite change from  $A$  to  $B$  or  $C$  to  $D$ .

The cycle traced in Figure 6 is equivalent to a Carnot cycle. Therefore,

$$dW = Q \frac{dT}{T}$$

But the work is also given by

$$dW = dP(\Delta V)$$

Combining and rearranging

$$\frac{dP}{dT} = \frac{Q}{T(\Delta V)} = \frac{\Delta H}{T\Delta V}$$

Where gases are involved, by assuming (1) the gas laws to apply and (2) the volume before the change negligible compared with that after, the approximate form

$$\frac{d \ln P}{dT} = \frac{\Delta H}{RT^2}$$

results. In this expression  $\Delta H$  is the enthalpy change for the process per mol of gas. If in addition the monovariant heat effect,  $\Delta H$ , be assumed constant, independent of temperature, the previous equation may be integrated, giving

$$\ln \frac{P_2}{P_1} = \frac{\Delta H}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

2. By combining the Clapeyron equation with Dühring's rule, derive the interesting and useful relation

$$\frac{\Delta H_A}{\Delta H_B} = \frac{T_A \Delta V_A}{T_B \Delta V_B} \frac{dT_B}{dT_A}$$

or if the gas laws, etc., may be assumed,

$$\frac{\Delta H_A}{\Delta H_B} = \frac{T_A^2}{T_B^2} \frac{dT_B}{dT_A}$$

where subscript  $A$  refers to a reference substance and subscript  $B$  to the substance under discussion.

3. The latent heat of fusion of acetic acid at its normal melting point,  $16.6^\circ\text{C}$ ., is  $44.7$  cal./gm. Assuming that the density of the solid is  $1.2658$  and that of the liquid is  $1.0493$ , at what temperature will acetic acid melt when the pressure is  $10$  atm.?

4. Calculate the difference in the entropy of  $1$  gram of water at  $0^\circ\text{C}$ ., and  $1$  gram of water at  $100^\circ\text{C}$ ., the pressure being constant at  $1$  atm. and the specific heat of water assumed  $1$ . Repeat for  $1$  lb. water and a temperature change from  $32^\circ\text{F}$ . to  $212^\circ\text{F}$ . Check your computation by means of the steam tables.

5. Derive a general expression for the change in entropy when  $1$  mol of a perfect

A ball of copper weighing  $7$  lb., at a temperature of  $850^\circ\text{F}$ ., is plunged into a vessel containing  $40$  lb. of water at a temperature of  $60^\circ\text{F}$ . Assuming the specific heat of copper as  $0.095$ , that of water as  $1$ , find the change in the entropy of (1) the (2) the copper, (3) the copper and water. Repeat the calculations with the originally the copper was  $200$  ft. above the water.

If the temperatures of the copper and water were reversibly equalized, how much work could be obtained?

7. A reversed Carnot engine is used for heating a building. The outside air at  $-10^{\circ}\text{F.}$  is the cold body; the building at  $70^{\circ}\text{F.}$  is the hot body, and 200,000 B.t.u./hr. are required for heating. Find (a) heat taken from outside per hour; (b) minimum horsepower required.

8. A heat exchanger is to be constructed in which air ( $M\bar{c}_p = 7.0$ ) is to be heated from  $20^{\circ}\text{F.}$  to  $150^{\circ}\text{F.}$  by a stream of air originally at  $300^{\circ}\text{F.}$  The molal ratio of heated air to heating air is unity.

(a) Calculate, on a basis of 1 mol of air heated, the change in entropy of the heated and the heating air on the assumption that the exchanger operates with (1) parallel flow and (2) countercurrent flow.

(b) What is the total entropy change for the two cases of (a)?

(c) What would have been the entropy change for each air stream had the exchanger operated countercurrently and with heating air entering at  $150^{\circ}\text{F.}$ ?

9. An insulated tank containing 1 mol of nitrogen at  $200^{\circ}\text{C.}$  and 50 atm. is connected, through a lagged pipe line and a valve, to a similar tank containing 2 mols of nitrogen at  $200^{\circ}\text{C.}$  and 10 atm. The valve is opened, and the two bodies of gas are allowed to mix adiabatically. Assuming that (1) the gases follow  $PV = NRT$ , and (2) Dalton's law for gas mixtures applies, what is the change in entropy, and what has changed in entropy?

10. Repeat Problem 9, assuming the second tank to have originally contained 2 mols of oxygen at  $200^{\circ}\text{C.}$  and 10 atm., instead of nitrogen.

11. Calculate the maximum work that could be obtained from the system undergoing the change outlined in Problem 10.

12. How would you determine the change in entropy for a chemical reaction taking place at  $20^{\circ}\text{C.}$  and 1 atm.?

13. A perfect gas originally at  $30^{\circ}\text{C.}$  and 10 atm. is allowed to undergo a Joule-Thomson expansion to 1 atm. abs. Calculate the change in entropy. Interpret your answer in the light of the second law teaching regarding the value of heat as influenced by its temperature level.

14. The following table ("International Critical Tables," Vol. 3, p. 372), gives the partial pressure of water vapor above a saturated solution of  $\text{NaNO}_3$ .  $C$  is grams of  $\text{NaNO}_3$  per 100 grams of water.

$t, ^{\circ}\text{C.}$	$p, \text{mm.}$	$C$	$t, ^{\circ}\text{C.}$	$p, \text{mm.}$	$C$
0	3.7	73.0	70	148.1	135.6
10	7.2	80.5	80	216.1	148.0
20	13.2	88.2	90	306	160.9
25	17.6	92.0	100	422	176.0
30	23.2	96.2	110	569	192.4
40	39.1	104.8	120	748	210.6
50	63.3	113.9	120.59	760	211.7
60	98.6	124.0	125	851	220.3

Compute approximately the heat of crystallization of  $\text{NaNO}_3$  at  $60^{\circ}\text{C.}$ , expressing your result in B.t.u. per pound of  $\text{NaNO}_3$ .

15. Chlorobenzene boils at  $131.68^{\circ}\text{C.}$ ; at  $70.3^{\circ}\text{C.}$  its vapor pressure is 100 mm. Calculate the heat of vaporization of chlorobenzene at  $130.6^{\circ}\text{C.}$  and compare with the value given in Perry's "Chemical Engineers' Handbook" (p. 453) of 77.59 gr. cal./gr.

## CHAPTER X

### INTERPRETATION OF THE SECOND LAW PRINCIPLE

Belief that energy cannot be created — the first law — was established by experiment. As a result of experiment, the second law leads to the conclusion that it is impossible to increase the ability of any system to do work except by taking work-producing ability from the surroundings. In any completely isolated system, capacity for doing work cannot be increased. At best, for reversible changes, it remains constant. This has led to the statement that our universe, if it is considered isolated, has a definite capacity for doing work, with reference to a chosen datum state, just as a wound-up spring, a lifted weight, or a charged storage battery. Since the stored work is being continually consumed, our universe would seem to be approaching ever closer to a state of no capacity for doing work. During this process the total amount of energy need not change. But energy without ability to perform work is of small value to mankind. For example, the "heat" of the oceans is a vast store of practically useless energy. Were it possible to increase the capacity of either an isolated system, or a system and its surroundings, to do work, this increase could be utilized to pump a quantity of heat uphill. The sole net result would be equivalent to a flow of heat from a lower to a higher temperature level — an impossible result.

### CALCULATION OF WORK EFFECTS

For some important types of processes the works obtainable are of such importance that special names have been given the expressions by which they are calculated. Since for any process it is the maximum or reversible effect which is unique, reversibility will always be assumed in the derivations to follow, unless otherwise stated. Moreover, further discussion will show that, in addition to adiabatic processes, those taking place either isothermally or with all heat transfer at a single fixed temperature are in general the most important for engineering work.

**Non-Flow Reversible Isothermal Processes.** It will be remembered that

$$\Delta S = \frac{Q_{rev.}}{T} \quad (1)$$

if the temperature is constant. Making this substitution in the usual first law expression  $Q - W = \Delta E$ , and rearranging,

$$-W_T = \Delta E - T\Delta S \quad (2)$$

If in addition the volume is constant (for instance, a chemical reaction taking place isometrically),

$$-W_{V,T} = \Delta E - T\Delta S \quad (3)$$

Since in this case no external mechanical work has been done, the  $-W_{V,T}$  referred to must be work of a non-mechanical nature, perhaps electrical work, which has left the system.

For constant-pressure, isothermal, reversible non-flow processes such as chemical reactions taking place in electrical cells, often open to the atmosphere, the work will in general be made up of two types: mechanical, done on the surroundings by a change in volume of the system; and electrical, done by the cell. The mechanical work at constant pressure is  $P\Delta V$ , where  $\Delta V$  is the total volume change of the system. This may here be written  $\Delta(PV)$

$$\text{Then} \quad -W_{P,T} = \Delta E - T\Delta S \quad (4)$$

$$-W_{P,T} = \Delta(PV) + W_e \quad (5)$$

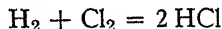
$$-W_e = \Delta E + \Delta(PV) - T\Delta S$$

$$-W_e = \Delta H - T\Delta S \quad (7)$$

The work, other than that done in allowing for the expansion (or contraction) of the system, need not necessarily be electrical, but in any event it may be thought of as the net or useful work effect

$$-W_{\text{net}, T, P} = \Delta H - T\Delta S \quad (8)$$

Some isothermal, reversible, non-flow changes may occur at both constant pressure and constant volume, as for instance the chemical reaction



For these

$$W_{P,T} = -W_{\text{net}, P, T} = -W_{V,T} \quad (9)$$

**Non-Flow Reversible Processes with Temperature Change.** Many important non-flow processes are not isothermal. In these, any heat rejected must be transferred at the lowest possible temperature *if maximum work is to be realized*. Heat rejected at a higher temperature could be converted in part to work by operating a heat engine between

this and the lowest temperature. In the limiting case the so-called "sink" to which this heat is rejected would be so large as to remain unchanged in temperature during transfer of heat to it. Practically this condition is closely approximated when heat is rejected from condensing steam to cooling water. As a matter of fact, our surroundings generally approximate a large isothermal sink, seasonal variations in temperature for the most part being useless for industrial work production.

The heat reversibly rejected to a sink at fixed temperature ( $T_0$ ) is

$$Q = T_0 \Delta S \quad (10)$$

where  $T_0$  generally differs from the system temperature ( $T$ ). The entropy change of the system is  $\Delta S$ .

By methods analogous to those used previously the following equations may be established:

(11)

$$-W_{\text{net}, P} = \Delta H - T_0 \Delta S \quad (12)$$

$$-W_{\text{net}, V} = \Delta E - T_0 \Delta S \quad (13)$$

**Effect of Potential, Magnetic, and Similar Forms of Energy.** All these are completely and quantitatively convertible to work and may be included in the preceding work equations by writing the general first law equation so as to account for them

$$Q - W = \Delta E + \text{Potential work} + \text{Magnetic work}$$

Such terms, when required, are understood to be added to the various work equations derived in this chapter. Often it is convenient to assume that these additional effects are included in the single term  $W$ . Either point of view is permissible, provided that one is consistent.

**Reversible Flow Processes.** Recall that the overall energy balance (the first law) for a flow process is:

$$Q - W_{\text{flow}} = \Delta H + \Delta \frac{U^2}{2g} + \Delta X \quad (14)$$

For reversible isothermal processes

$$Q = T \Delta S \quad (15)$$

Substituting this expression in the preceding equation yields

$$-W_{T, \text{flow}} = \Delta H - T \Delta S + \Delta \frac{U^2}{2g} + \Delta X \quad (16)$$

or where the potential and kinetic energy changes are either absent or negligible

$$-W_{T, \text{flow}} = \Delta H - T \Delta S \quad (17)$$

For *reversible non-isothermal processes* where all heat is transferred at fixed sink temperature,  $T_0$ , the overall energy balance is

$$-W_{\text{flow}} = \Delta H - T_0 \Delta S + \frac{\Delta U^2}{2g} + \Delta X \quad (18)$$

or where kinetic and potential energy effects may be disregarded

$$-W_{\text{flow}} = \Delta H - T_0 \Delta S$$

### FREE ENERGY AND AVAILABILITY

So important are some of the preceding expressions that special names have been given them.

**Free Energy.** For any isothermal, constant-pressure, reversible, non-flow process, or for any isothermal, reversible flow process, the net work available is given by the expression

$$-W_{\text{net}, T} = \Delta H - T \Delta S \quad (20)$$

Correction for kinetic energy and similar effects where necessary is made by adding the appropriate terms. An important and useful function is mathematically defined by the equation

$$F = H - TS \quad (21)$$

This function  $F$  is called the free energy. For an isothermal process, change in free energy is

$$\Delta F = \Delta H - T \Delta S \quad (22)$$

It is important to note that for a reversible, isothermal, constant-pressure, non-flow process

$$\Delta F = -W_{\text{net}, T, P} \quad (23)$$

For *any* reversible, isothermal flow process

$$\Delta F = -W_{\text{flow}, T} \quad (24)$$

**Availability.** Mathematically it may be said that

where  $B$  is defined as the availability and  $T_0$  is a fixed temperature usually referred to as the dead-state temperature and in general not the temperature ( $T$ ) of the system. For any process change in availability is

$$\Delta B = \Delta H - T_0 \Delta S \quad (25)$$

For constant-pressure, reversible, non-flow processes, if all heat transfer is at the fixed temperature  $T_0$

$$-W_{P, \text{net}} = \Delta B = \Delta H - T_0 \Delta S \quad (27)$$

For reversible, flow processes if all heat transfer is at the fixed temperature  $T_0$

$$-W_{\text{flow}} = \Delta B = \Delta H - T_0 \Delta S \quad (28)$$

The availability of a fluid in continuous flow is "the maximum amount of useful work which any heat engine, however simple or complex, can deliver against outside forces, to a shaft, by changing the condition of the flowing fluid to the dead state where  $P = P_0$ ,  $T = T_0$ , and  $U$  (velocity)  $= 0$ ."<sup>1</sup> In most general terms the dead state of a substance may be defined as that condition in which not only pressure and temperature but also chemical and all other potentials are balanced — an idea which is readily seen to coincide with that for equilibrium. The "dead state" practically always infers a condition of zero velocity. It is instructive to note that a system containing a fluid at a temperature less than the dead-state temperature may have a positive availability. Work can be obtained by returning the fluid to the dead state just equivalent to that necessary to bring the fluid to its previous condition below the dead state.

**Another Work Function.** There is a third common thermodynamic function defined as

$$A = E - TS \quad (29)$$

For an isothermal, reversible, non-flow process

$$\Delta A = \Delta E - T \Delta S = -W \quad (30)$$

If in addition the process is isometric

$$-W_{\text{net}, T} = -W_{T, V} = \Delta A = \Delta E - T \Delta S \quad (31)$$

This difference,  $\Delta E - T \Delta S$ , is sometimes called the free energy change, an unfortunate circumstance since, in this country, the free energy is usually defined as:

$$F = H - TS$$

To avoid confusion, the term *free energy* will always be reserved for the latter function. The two functions  $F$  and  $A$  bear the same relation to each other as  $H$  and  $E$ .

**General Characteristics of the More Important Work Functions.** Since each of the functions  $A$ ,  $B$ , and  $F$  is a difference between two point functions, each must be a point function, a property of the state of the



system, and, unlike work (in general) and heat, independent of the path. Consequently, derivatives of these functions will exhibit the properties mathematically ascribed to a complete or perfect differential.

**Engineering Importance of the Various Work Functions.** Broadly speaking, practically all important industrial processes start and end at essentially the same temperature. In making sulfuric acid, the sulfur, air, and water enter the process at atmospheric pressure and temperature. The finished acid leaves at the same pressure and temperature. In a well-operated plant, the coal, water, and air enter at about the same temperature and pressure as the cooling water leaves. To be sure, the flue gas leaves at a higher temperature, but in the limiting case this would be reduced to that of the surroundings by heat exchange against the incoming fuel, water, and air (or theoretically by operating a reversible Carnot heat engine between the gas and the surroundings). In the actual process, economics alone dictate how much the flue-gas temperature shall be reduced. In addition, practically all our usable stores of energy are essentially at the temperature and pressure of the surroundings. As they are used, this is true of the more important ones: coal, petroleum, and natural gas. Since energy available as water power is entirely work, it need not concern us in this discussion.

It is not unreasonable to consider most of the industrially important processes as starting and ending at the same pressure and temperature even though the changes themselves are far from isothermal and isobaric.

Previously, an expression,

$$\Delta F = \Delta H - T\Delta S$$

was derived for isothermal reversible changes. This was found to be a point function and as such is applicable for evaluating the net reversible work evolution, or requirement, of industrial processes even though actually they may not be isothermal. For flow processes, equality of initial and final temperatures is sufficient; for non-flow processes, in addition, the initial and final pressures must be the same.

Often in a process the temperature at the start is far different from that at the end. A turbine stage where the entering steam is at a different temperature and pressure from that leaving offers a good example. In its passage through the stage the fluid has lost ability to do work while the turbine actually has done work on the surroundings, *i.e.*, through the rotating shaft. If the process has been reversible, the steam lost an ability to do work exactly equal to the work done. A : example is afforded by an evaporator in which steam is supplied

at one temperature and exhausted at another. In such cases it is the availability change

$$\Delta B = \Delta H - T_0 \Delta S$$

rather than the free energy change

$$\Delta F = \Delta H - T \Delta S$$

which is of importance.

From the viewpoint of the first law, a thermodynamic analysis need include only an overall energy balance; from the second law, one must also include a "work balance." A process would have a maximum efficiency according to the first law if energy input were exactly equal to recoverable energy output, there being none of the usual radiation, convection, and similar losses. Considered in the light of the second law, maximum efficiency is attainable (reversibility) only if, at the completion of the process, all energy involved has an ability to do work exactly equal to that before the change took place.

To evaluate any process properly, it must be examined in the light of both laws.

TABLE I  
SUMMARY OF SOME REVERSIBLE WORK EFFECTS

Process	Conditions of Restraint	Reversible Work Effect (Neglecting kinetic, potential, and similar effects)	Change in Corresponding Thermodynamic Function
Non-flow	Reversible, isothermal	$-W_T \quad \Delta E - T \Delta S$	$\Delta A = \Delta E - T \Delta S$
	Reversible, isothermal, constant-pressure	$-W_{net, P} = \Delta H - T \Delta S$	$\Delta F = \Delta H - T \Delta S$
Non-flow	Reversible, isothermal, constant-volume	$-W_{net, V} = \Delta E - T \Delta S$	$\Delta A = \Delta E - T \Delta S$
Non-flow	Reversible, heat transfer at $T_0$	$-W = \Delta E - T_0 \Delta S$	
Non-flow	Reversible, constant-pressure, heat transfer at $T_0$	$= \Delta H - T_0 \Delta S$	$\Delta B = \Delta H - T_0 \Delta S$
Flow	Reversible, isothermal	$-W_{net, T} = \Delta H - T \Delta S$	$\Delta F = \Delta H - T \Delta S$
Flow	Reversible, heat transfer at $T_0$		$\Delta B = \Delta H - T_0 \Delta S$

**Entropy and Unavailable Energy.** A review of the past several pages cannot fail to impress one with the importance of entropy change as an index of the amount of energy made unavailable in any process. Some

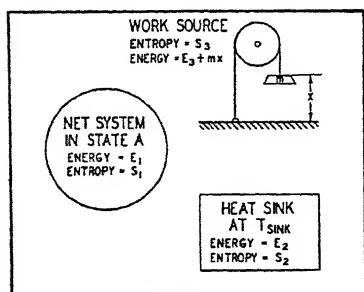
study will make it clear that *for reversible processes any system and its surroundings suffer no entropy change*, while for all actual processes there must be a net increase in entropy, even though some part of the system or surroundings may show a decrease. Thus, in the transfer of heat from a hot to a cold body, the "entropy decrease of the hot body," when heat is transferred from it, is  $\Delta S_1 = \int dQ_{\text{rev.}}/T_1$ . This same quantity of heat when picked up by the cooler body must be at a lower temperature,  $T_2$ ; otherwise, no actual transfer could have occurred. The "entropy increase" suffered by the colder body will be  $\Delta S_2 = \int dQ_{\text{rev.}}/T_2$ . It is mathematically impossible for  $\Delta S_2$  to be equal to or smaller than  $\Delta S_1$ , because  $T_2$  is less than  $T_1$ . Moreover, the energy at  $T_2$  now has less value for producing work than when at the higher temperature  $T_1$ , as pointed out in the discussion of the previous pages. The actual transfer of heat is then a process involving an entropy increase, a decrease in ability of the energy under discussion to do work.

It is interesting to note that as the energy left the hot body it could not foretell whether it was to suffer a net entropy increase, decrease, or even to undergo a reversible transfer. As far as the hot body was concerned, the entropy change would have been the same had the transfer been to a body but differentially cooler, *i.e.*, a reversible transfer. Considering only the cold body, similar reasoning applies. It is only by examining the overall effect that complete understanding is obtained. The system composed of the two bodies has undergone an increase in entropy. Had the heat,  $Q$ , been transferred from  $T_1$  to  $T_2$  reversibly, through a heat engine, a quantity of work would have been collected. Since this was not done the chance to realize this work is forever lost.

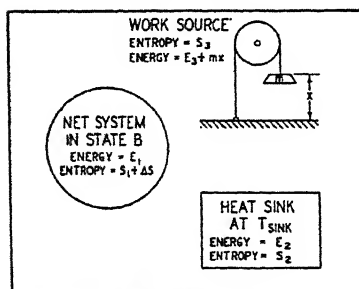
Had the heat transfer been truly reversible, at no point would the temperature difference have been more than differential. Under these conditions the entropy change for the complete process — both system and surroundings — is zero.

To arrive at a quantitative expression for the relation between entropy change and loss in ability to do work, consider any system and its surroundings (Figure 1). Let these together be called the "net system." In addition, assume a source of work (perhaps a lifted weight) and an isothermal sink at temperature  $T_{\text{sink}}$  to which heat may be transferred. The "net system" plus the work source and heat sink may be thought of as a "gross system." Let any conceivable irreversible change occur in the net system (intermediate state). The net system may be restored to its original condition by expending work (from the lifted weight). If restoration is by a reversible path, a minimum of "extra" work will be required. But, in addition, energy as heat must pass from the net system to the external sink exactly equal in amount to

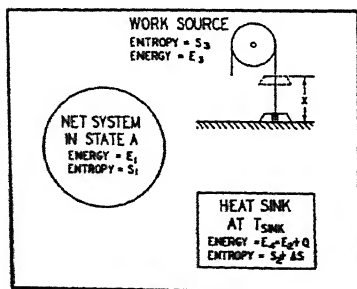
the work added; otherwise, the energy content of the net system after restoration would not be the same as before any change occurred (final state).



ORIGINAL STATE



INTERMEDIATE STATE



FINAL STATE

FIG. 1. Interpretation of Entropy Increase.

To be sure that any heat transferred will be useless, it should leave at the *lowest temperature available* for heat discard,  $T_{\text{sink}}$ . During the reversible restoration previously mentioned, an entropy change  $\Delta S$  would occur in the net system exactly equal, but of opposite sign, to that experienced by that same system in the original irreversible change. Under the above conditions, the heat ( $Q$ ) to be transferred from the net system, for a minimum of restoration work, is  $-T_{\text{sink}}\Delta S$  and this must be equal to the restoration work ( $W$ ).

During engineering processes heat discard is usually either to cooling water or to the atmosphere. These may be thought of as sinks so large that heat rejection to them causes no appreciable change in their temperatures. For actual (irreversible) processes, loss in available energy (ability to do work) may be calculated by the expression:

$$T_0 \Delta S_{\text{net}}$$

where  $T_0$  = temperature of atmosphere or cooling water, in most cases of engineering importance.

$\Delta S_{\text{net}}$  = algebraic sum of entropy changes in system and surroundings.

In any process, the loss in available energy is given by the change in entropy multiplied by the lowest temperature available for heat discard from the system.

For evaluation of net loss in ability to do work, suffered by any system and its surroundings, the net change in entropy of the two is to be used. For evaluation of the decrease in free energy or availability, of any system, the change in entropy of the system is to be employed. As far as the system is concerned, it has lost an ability to do work irrespective of whether the work ability is stored in the surroundings, the reversible case, or lost either in whole or part, the various irreversible cases.

The utility of the entropy function for the mechanical engineer is evident. He must consider, especially in engines, processes which are often approximately adiabatic and reversible.

On the other hand, the free energy or availability functions are of greater utility to the chemical engineer. Moreover, they are more convenient, because, in their evaluation, one need consider only the system; whereas for calculation of net entropy changes, except for adiabatic cases, both the system and the surroundings must be kept in mind.

## SECOND-LAW ANALYSIS OF IRREVERSIBLE PROCESSES

Although a few industrial processes approach reversibility, by far the majority are highly irreversible. A general analysis, in terms of entropy, was presented for these in the preceding sections. Here a more detailed study will be made from a somewhat different viewpoint.

**Method of Analysis.** To aid in clearly understanding many of the relations presented in this part, it is well to think of an irreversible process as occurring at each differential step reversibly, this being immediately followed by an irreversible step of such magnitude that the system during its change does follow the path actually under discussion. For any reversible non-flow process

$$dE = dQ -$$

But for *any* non-flow process it may be said

$$dE = dQ - dW_{\text{actual}} \quad (32)$$

$$dE = dQ - dW_{\text{rev.}} + dL \quad (32a)$$

It follows that

$$dW_{\text{actual}} + dL = dW_{\text{rev.}}$$

A little thought will lead to the conclusion that for actual processes  $dL$  is essentially positive. For reversible processes it becomes zero. The term  $\int dL$  will represent the loss in ability to do work because of the irreversible nature of the process

For any steady-flow process

$$dE = dQ - dX - d\left(\frac{U^2}{2g}\right) - d(PV) - dW_{\text{shaft}} \quad (34)$$

If  $dE$  and  $dQ$  are at every stage the same for the non-flow and flow processes one may substitute for  $dE$  in Equation 34 its equivalent  $dQ - dW_{\text{rev.}} + dL$  from Equation 32a. Then

$$-dW_{\text{rev.}} + dL + dX + d\left(\frac{U^2}{2g}\right) + d(PV) + dW_{\text{shaft}} = 0 \quad (35)$$

Integrating between the limits corresponding to the initial and final states,

$$-W_{\text{rev.}} + L + \Delta X + \Delta\left(\frac{U^2}{2g}\right) + \Delta(PV) + W_{\text{shaft}} = 0 \quad (36)$$

When only mechanical work effects are of importance

$$W_{\text{rev.}} = \int P dV$$

and the preceding equation may be written

$$L + \Delta\left(\frac{U^2}{2g}\right) + \Delta(PV) + W_{\text{shaft}} = 0 \quad (37)$$

For non-flow processes where only mechanical work effects are of importance

$$W_{\text{actual}} + L = \int P dV \quad (38)$$

Note that  $\int P dV$  is to be evaluated along the actual path followed, irrespective of whether the process is reversible or not. To compute  $\int P dV$ , values of the *actual* pressures and volumes of the working fluid during the change must be used — the surroundings are ignored. For illustration, direct attention to one mol of a perfect gas expanding isothermally in a horizontal cylinder and moving a piston which eventually comes to rest against a stop. To simplify discussion let the space beyond the piston face be evacuated. No work is done on the surroundings,  $W_{\text{actual}} = 0$ . But

$$= -RT \ln \frac{P_2}{P_1}$$

$P_2$  = final pressure of gas in cylinder.

$P_1$  = initial pressure of gas in cylinder.

$$-RT \ln \frac{P_2}{P_1} = L$$

$\therefore T\Delta S$  for the system and surroundings.

The term  $L$  is often called the friction. Since in mechanical processes lost work practically always appears as heat which is dissipated to the surroundings without useful effect, in such processes it is customary to interpret  $L$  as energy originally available for doing work but now converted to heat. In any process  $L$  is that part of the possible work effect which has been lost because of irreversibility.

**Evaluation of  $\int P dV$  in Actual Flow Processes.** For irreversible flow processes, difficulty often arises because the actual path is unknown.

Thus the conditions at entrance and exit for a fluid flowing through a pipe line may be known but practically none of the conditions along the pipe.

In such cases a reasonable path must be assumed between the initial and final states. Where assumption is necessary, practically always the flow is considered either isothermal or adiabatic.

**Bernoulli's Theorem.** Considering Equation 37, it is evident that the first and fifth terms may be combined, giving

$$\int V dP + L + \Delta X + \Delta \left( \frac{v^2}{2g} \right) + W_{\text{shaft}} = 0 \quad (39)$$

Equation 39, applicable to any steady-flow process when work effects are mechanical, is called *Bernoulli's theorem*.

It is a fundamental relation in the study of fluid flow.

The practice (especially in hydraulics) of taking unit amount (e.g., 1 lb. of material) as the basis for writing this equation and then expressing all terms as foot-pounds results in the units of each term becoming *foot-pounds of energy per pound of fluid flowing* or feet of fluid flowing. The various terms are then referred to as heads — velocity head, potential head, pressure head. This may lead to confusion unless one distinctly remembers that *each term is an energy term*.

Bernoulli's theorem is of such industrial importance that discussion in a separate chapter is advisable.

#### A Graphical Interpretation.

Reference to Figure 2<sup>1</sup> makes possible visualization of many of the necessary relationships discussed in the preceding several paragraphs. Assume all work effects mechanical.

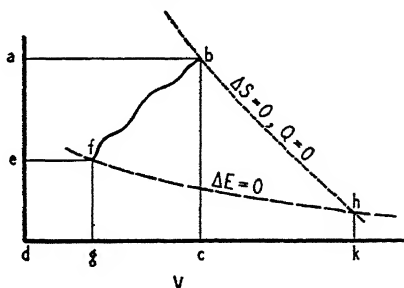


FIG. 2. Graphical Relations between Work and Heat Effects.

<sup>1</sup> Private communication from J. A. Beattie.

Let the curve  $f-b$  be the actual  $P-V$  path followed by a fluid in going from initial state  $f$  to final state  $b$ . For *any* process the area  $gfbc$  represents the value of  $\int P dV$ . If the process be non-flow and reversible this area represents the work done on the surroundings. If the process is reversible and of a steady-flow type, the work done on the surroundings is  $P_1 V_1$  (area  $efgd$ ) plus  $\int P dV$  (area  $gfbc$ ) minus  $P_2 V_2$  (area  $abcd$ ). But the geometry of the figure indicates that the algebraic sum of these three work effects is represented by area  $(efba)$ . For any process, reversible or not, area  $efba$  represents  $-\int V dP$ . For reversible steady flow  $-\int V dP$  is the net or shaft work done on the surroundings.

A reversible adiabatic through point  $b$  will intersect at  $h$  a constant internal energy line through point  $f$ . Area  $cbhk$  represents  $\Delta E$  for the process indicated by the curve  $f-g$ , whether the process is reversible or irreversible, flow or non-flow. If the change  $f-g$  is reversible, whether flow or non-flow, area  $gfbhk$  represents the heat added.

For irreversible processes graphical visualization of  $Q$  is not so easy. If any curve between  $f$  and  $b$  is drawn such that the area between it and the  $V$  axis is equivalent to the actual irreversible non-flow work done, then this area plus area  $cbhk$  will be the heat added whether the process is flow or non-flow.

It is instructive to compare this graphical interpretation with the argument immediately following Equation 34.

### SUMMARY

1. The importance of considering all energy from the viewpoint of its availability or ability to do work was emphasized. This is, broadly speaking, a teaching of the second law.
2. The reversible work effects for several important processes are summarized in Table I.
3. The greater utility of the free energy function as contrasted with the more general entropy concept was emphasized.
4. A method for evaluating loss in capacity to do work for any system because of any kind of change was developed. This loss is equal to

where  $T_0$  is the lowest temperature available for heat discard and  $\Delta S_{\text{net}}$  is the change in entropy of system and surroundings.

5. An alternative method of analyzing irreversible processes was presented. Instead of direct use of entropy change this includes a term  $L$  defined as loss in available energy suffered because of the process. For mechanical flow processes  $L$  was shown to be the term usually known as friction.



## NOTATION FOR CHAPTER X

$A$	Helmholtz free energy ( $E - TS$ )
$B$	Availability ( $H - T_0S$ )
$E$	Internal energy
$F$	Free energy ( $H - TS$ )
$H$	Enthalpy
$L$	Lost available energy due to irreversibility
$P$	Absolute pressure
$Q$	Heat withdrawn from surroundings
$S$	Entropy
$T$	Absolute temperature
$U$	Velocity
$V$	Volume
$W$	Work done by the system
$X$	Height above datum plane

*Subscripts:*

$e$	non-mechanical
$P$	constant pressure
$T$	constant temperature
$V$	constant volume
$0$	refers to dead state, as $T_0$ , $P_0$ , $X_0$ .

*Greek Letters:*

$\Delta$	(Value in final state) — (Value in initial state)
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## PROBLEMS

NOTE: It is suggested that changes in entropy and, where possible, availability and free energy be calculated for problems previously given.

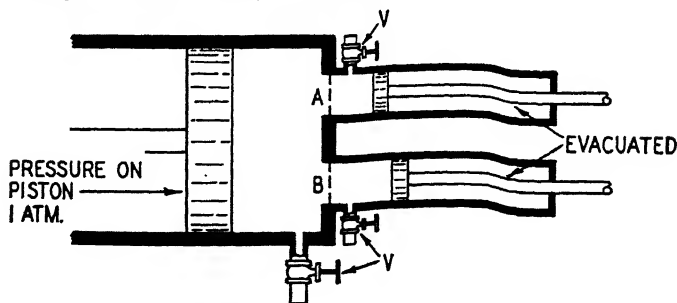


FIG. 3.

1. Calculate the minimum isothermal work required to produce 32 lb. of oxygen at 1 atm. and 20°C. from air at the same pressure and temperature, the nitrogen being discarded to the atmosphere.

*Solution.* To aid in visualization when solving problems of this type it is often convenient to assume the existence of suitable semipermeable membranes. In the preceding figure of a theoretical device to carry out the proposed process,  $A$  is a

membrane permeable to oxygen only and  $B$  is a membrane to pass nitrogen only. At points marked  $V$ , suitable valves are provided, and all processes are to be reversible and isothermal.

The various steps are as follows:

1. Draw out the large piston filling the cylinder with air at 1 atm. and  $20^\circ\text{C}$ ., the gas entering through the valve in the cylinder side. Sufficient air is to be drawn in so that the cylinder contains 32 lb. of oxygen (and also  $\frac{3}{4}(28) = 105$  lb. of nitrogen).

The net reversible isothermal work for this step is zero.

2. Push in the large piston, the gases being exhausted through membranes  $A$  and  $B$ . The total pressure in the cylinder is to be always exactly 1 atm., and under these conditions the oxygen leaving through  $A$  will be at 0.21 atm. while the nitrogen leaving at  $B$  will be at 0.79 atm. The oxygen is now in the upper small cylinder at 0.21 atm. pressure while the nitrogen is in the lower at 0.79 atm. pressure. As for the large piston, the net work expended on it for the separation is zero. A certain work effect,  $0.21 V_1$ , has been done on the upper small piston, and another,  $0.79 V_3$ , has been done on the lower small piston.

3. The nitrogen may now be discarded to the atmosphere (through a membrane) by pushing in the lower small piston and expending a work effect  $0.79 V_3$  which exactly offsets the work previously done on this piston. The upper small piston must now be pushed in to compress the 32 lb. of oxygen from 0.21 atm. to 1.0 atm., the final condition. This work is  $RT \ln \frac{P_2}{P_1} = (1.99)(293)(2.3) \log \frac{1}{0.21} = 910 \text{ C.h.u.}$

To remove the compressed oxygen from its cylinder will require a work expenditure of  $1.0 V_2$ , but since the processes are isothermal and the gas laws assumed this effect exactly offsets the  $0.21 V_1$  previously mentioned.

Summing up, the net reversible isothermal work expenditure is

$$NRT \ln \frac{P_2}{P_1} = (1)(1.99)(293) \left( 2.3 \log \frac{1}{0.21} \right) = 910 \text{ C.h.u.}$$

Note, in addition, that the assumed apparatus is now in its original state; it has passed through a cycle. The work effect calculated is a flow or shaft work. Moreover, the same result would have been obtained in any other type of apparatus similarly operated.

2. A flue gas containing 18 per cent  $\text{CO}_2$  and no  $\text{CO}$ , made by burning practically pure carbon, is being used in the manufacture of compressed carbon dioxide gas. The finished product is stored in steel containers under a pressure of 25 atm. abs. The exhausted gas, containing 7 per cent  $\text{CO}_2$ , and a negligible amount of water, leaves the lye absorbers and is discharged to the atmosphere.

Estimate, per 100 cu. ft. of  $\text{CO}_2$  at  $20^\circ\text{C}$ . and 25 atm., the minimum theoretical work consumption and the minimum theoretical carbon consumption.

3. Referring to Problem 20, Chapter VI, what is the minimum isothermal work of decomposition per cell assuming the water to enter at 160 lb./sq. in. abs. and the gases to leave at the same pressure? What is the thermodynamic or second law efficiency for the process? What is the entropy change for the chemical reaction taking place?

4. A plant is producing from air oxygen and nitrogen, each at 1 atm. and  $20^\circ\text{C}$ . What is the minimum theoretical pressure to which the air entering the system must ; this compression the only work input?

5. Derive a general equation for the flow work of isothermal reversible compression for a system composed of perfect gases which react as compression proceeds.

6. Sodium chloride is being separated from a 1 per cent solution of the salt in water. At 100°C. the vapor pressure over NaCl solutions is:<sup>1</sup>

gm. NaCl/100 gm. H <sub>2</sub> O	Density	<i>p</i> , mm. Hg
0	0.9584	760.0
5.82	1.0035	734.9
11.55	1.0432	709.7
17.05	1.0816	681.3
22.57	1.1202	652.9
27.99	1.1599	624.4

The solubility of NaCl at 100°C. is 39.22 gm. /100 gm. H<sub>2</sub>O.

Estimate the minimum theoretical work required for the separation of the salt from 10 tons of solution at 100°C.

(a) If the water is recovered as liquid water at 100°C.

(b) If the water is discharged as steam (at  $\frac{3}{4}$  atm. and 100°C.) for low-pressure heating.

7. The vapor pressure of ammonia and water over aqueous solutions of the gas at 20.0°C. is given by the following table:<sup>2</sup>

gm. NH <sub>3</sub> /1000 gm. H <sub>2</sub> O	, mm. Hg	mm. Hg
0	0.0	17.5
20	12.0	17.1
25	15.0	17.0
30	18.2	16.9
40	24.9	16.7
50	31.7	16.5
75	50.0	15.9
100	69.6	15.3
150	114	14.1
200	116	12.9
250	227	11.6
300	298	10.5

(a) Compute the net isothermal reversible work necessary for the separation by distillation of 100 lb. of a 20 per cent ammonia solution at 20°C. into ammonia gas at 1 atm. and liquid water at 1 atm.

8. On a day when the temperature is at 80°F. with a relative humidity of 70 per cent, an air-conditioning unit is delivering air at 60°F., 40 per cent relative humidity. The conditioning unit operates on the usual refrigerating dehydrating cycle. Per 100,000 cu. ft. of conditioned air delivered, what is the minimum theoretical work input to the system?

9. Derive a general expression for the minimum work consumption for isothermally separating any volatile binary mixture into its components.

10. Repeat the preceding problem on the assumption that Raoult's law may be applied.

<sup>1</sup> Swietoslawski, *Bull. soc. chim.* (4), 37, 263 (1925).

<sup>2</sup> Sherwood, *Ind. Eng. Chem.*, 17, 745 (1925).

11. How, from a thermodynamic point of view, would you evaluate the following?

- (a) Water at 1000 lb./sq. in. abs. and 100°F.
- (b) Steam at 10 lb./sq. in. abs. and 600°F.
- (c) Flue gas at 1 atm. and 600°F. containing 79 per cent  $N_2$ , 14 per cent  $CO_2$ , and 7 per cent  $O_2$ .
- (d) An oil at 600°F., 1 atm. (sp. ht. = 0.7).

## CHAPTER XI

### FLUID FLOW

The flow of liquids and gases through industrial equipment is an operation particularly suited for thermodynamic interpretation, and indeed such study has contributed in no small degree to the high efficiency with which fluids are moved through modern equipment. Steady flow and absence of chemical reaction will be assumed throughout the argument to follow. Moreover, the flowing material is assumed homogeneous and continuous. Flow of such mixtures as liquid drops in gas, gas bubbles in liquid, solids in gas or liquid is not only complex but beyond the scope of this discussion.

**Analysis of the Problem.** Three basic principles are to be kept in mind:

1. *The material balance.* As used for steady flow this is called the continuity equation. It is a statement that all matter passing any chosen section must pass every other. For utility this fact is sometimes presented in an alternative manner. Let  $(m/\theta)$  be the mass rate of fluid flow and  $U$  the linear velocity of flow. The cross-sectional area of the conduit through which flow is taking place is  $A$ , and the specific volume of the fluid  $V$ . The latter two refer to any particular location in the apparatus and may vary point to point.

$$\frac{m}{\theta} = \frac{UA}{V} \quad (1)$$

But

$$\left(\frac{m}{\theta}\right)_1 = \left(\frac{m}{\theta}\right)_x$$

$$\frac{U_1 A_1}{V_1} = \frac{U_x A_x}{V_x} \quad (2)$$

2. The *overall energy balance* for a steady-flow process

$$Q - W = \Delta E + \Delta(PV) + \Delta \frac{U^2}{2g} + \Delta X \quad (3)$$

3. The *second law*, available energy, balance for steady flow

$$\int P dV - W_{\text{shaft}} = \Delta(PV) + \Delta \frac{U^2}{2g} + \Delta X + L \quad (4)$$

At any point all three of these requirements must be fulfilled.

**Interpretation of the Problem.** The idea that the mode of flow may assume at least two quite different aspects is so universal that interpretation of flow phenomena is practically always postulated on such an understanding. As any fluid moves along a pipe, at very low velocities it may be visualized as a series of liquid tubes one fitting within the other, the outer, in contact with the retaining wall, moving exceedingly slowly and each succeeding inner tube moving somewhat faster than its outside neighbor — a quite orderly motion without too much interference between adjacent tubes. Because of the important role played by viscosity in this type of flow it is called viscous or sometimes streamline flow.

With a given fluid and apparatus, as the velocity is increased a condition is reached where, if some type of visual indicator, such as suspended aluminum particles, is present, considerable mixing and interference between the various tubes are evident. A high degree of turbulence develops, and the flow is known as turbulent. Within the range of industrially important velocities, additional increases bring about no further radical changes in the type of flow.

**Friction to Flow in Straight Uniform Pipes.** It may be shown that for a pound of fluid passing through a straight uniform pipe the loss in available energy due to friction is

$$L = \frac{2flU^2}{gD} \quad (5)$$

where  $L$  = foot-pounds per pound of fluid flowing.

$f$  = an empirically determined constant.

$l$  = length of pipe (equivalent), feet.

$U$  = Average linear velocity of flow, feet per second.

$g$  = gravitational constant, 32.2 feet per (second)<sup>2</sup>.

$D$  = pipe diameter, feet.

This is the Fanning equation.

Experimentally it is found that values of  $f$  may be well correlated by plotting against the dimensionless ratio,  $DU\rho/\mu$ , in which  $D$  and  $U$  are expressed in units given previously while  $\rho$  is the density (lb./cu. ft.) and  $\mu$  is the viscosity (lb.)/(sec.) (ft.) (for the English system of units). The group  $DU\rho/\mu$  is called the Reynolds number.<sup>1</sup> A plot of Reynolds number versus  $f$  gives the simple curve of Figure 1.<sup>2</sup> For all values of  $DU\rho/\mu$  to the left of 2100, flow is viscous; to the right, it is assumed turbulent.

<sup>1</sup> Viscosity values are often reported in centipoises. These are converted to (lb.)/(sec.) (ft.) by multiplying by 0.000672. Since the Reynolds number is dimensionless, any consistent system of units may be used.

<sup>2</sup> Based on correlation of Drew, Koo, and McAdams, *Trans. Am. Inst. Chem. Engrs.*, 28, 56 (1932). Also see Drew and Genereaux, *Trans. Am. Inst. Chem. Engrs.*, 32, 17 (1936).

## FRICTION TO FLOW IN STRAIGHT UNIFORM PIPES

For processes where mechanical effects only are of importance, as is true in ordinary fluid flow

$$-W_{\text{shaft}} = \int \frac{U^2}{2g} + \frac{U^2}{gD} \quad (6)$$

This equation is of general utility in solution of problems pertaining to flow of homogeneous fluids in pipes.

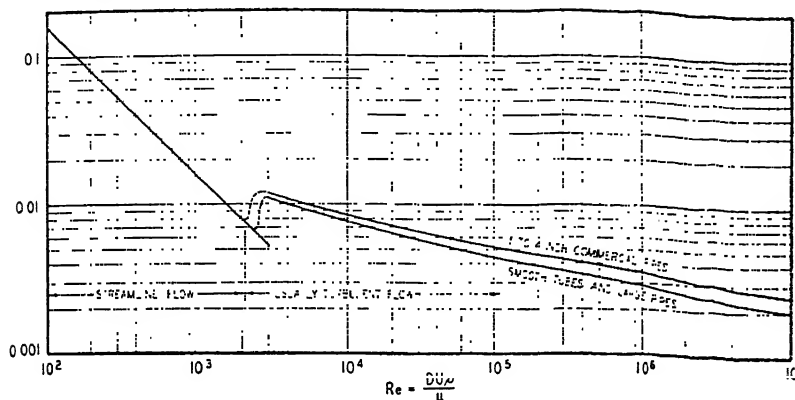


FIG. 1. Plot of Friction Factor versus Reynolds' Number.

Equation 6 may be derived from Newton's laws of motion. To simplify discussion assume the flow to take place in a straight uniform pipe. Let  $dF$  be the force acting to cause flow and  $dR$  the retarding frictional force. Then across any differential element of fluid,  $dm$ , with a length  $dy$ ,

$$g(dF - dR) = dm \frac{dU}{d\theta} \quad \longrightarrow \quad \begin{array}{c} \xrightarrow{dR} \\ \boxed{\phantom{0}} \\ \xleftarrow{F + dF} \end{array}$$

But

$$dF = (P - P - dP)A = -A dP$$

$$\frac{dy}{d\theta} = U; dm = \frac{A dy}{V}$$

Therefore

$$-gA dP - g dR = \frac{A}{V} d \left( \frac{U^2}{2} \right)$$

Divide by  $Ag$  and multiply by  $V$

$$-V dP - \frac{V}{A} dR = d \left( \frac{U^2}{2g} \right)$$

But

$$\frac{V dR}{A} = dL$$

Thus

$$-V dP = d \left( \frac{U^2}{2g} \right) + dL$$

If work is added and in addition there is a difference of level between the two sections under discussion, appropriate terms to account for these must be added.

$$-V dP = d\left(\frac{v^2}{2g}\right) + dL + dX +$$

**Other Factors Influencing Friction.** Roughness of pipe interior, presence of slime, dirt, or scale, or obstructions of any sort influence flow. These are either neglected or allowed for by introducing an engineering factor for safety.

Pipe irregularities of any sort, valves, ells, tees, enlargements, or contractions, lead to increased friction loss. Instead of calculating the influence of these directly, various empirical relations are used. These often express friction loss as that equivalent to additional lengths of pipe. The equivalent pipe length to be used in Equation 6 is the sum of the actual and the assumed additional pipe length.<sup>1</sup>

### MEASUREMENT OF FLOW FLUID

**Definitions.** A pressure gage connected to an opening in a surface along which a fluid glides without change in direction will read the *static pressure*. (Figure 2.)

If a tube bent at the lower end is placed facing into the moving stream, a gage attached to its upper end will read the *impact pressure*.

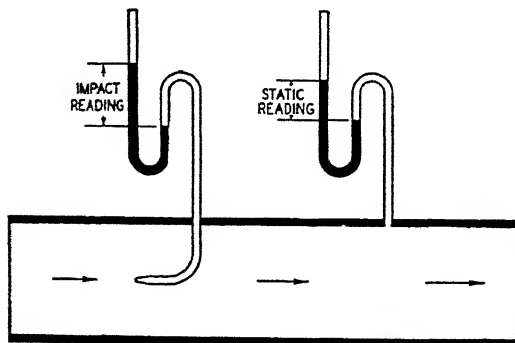


FIG. 2. Diagram Showing Static and Impact Pressures.

On the other hand, if this tube is moved with the flowing stream and at a velocity equal to the fluid velocity the gage attached to it will read the static pressure, as did the gage first mentioned.

The velocity pressure is the difference between the impact pressure and the static pressure.

$$\text{Impact pressure} - \text{Static pressure} = \text{Velocity pressure}$$

<sup>1</sup> For detailed discussion of these corrections see Walker, Lewis, McAdams, and "Principles of Chemical Engineering," New York, McGraw-Hill, 1937.



**The Pitot Tube.** An arrangement of two tubes and a manometer as shown in Figure 3 makes possible determination of velocity pressures set up by a flowing stream. For convenience, in a commercial Pitot

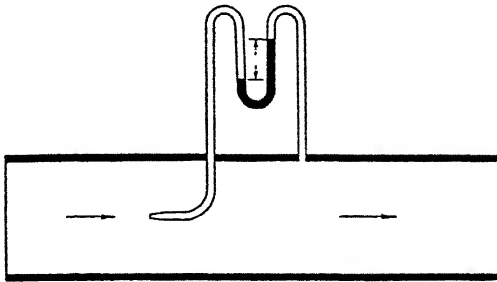


FIG. 3. Connections for Measuring Velocity Pressure.

tube the two tubes are arranged concentrically, the inner being the impact tube; the outer, closed at the lower end and perforated, serving as the static tube, Figure 4.

Fluid striking the end of the impact tube has its direction quickly changed to that at right angles to the original. This deflection develops a pressure at the tube mouth equivalent to that produced by destruction of the longitudinal velocity of the fluid filament striking the tube end. This is in addition to the static pressure at this point. By connecting the Pitot tube to opposite sides of a manometer the resulting manometric reading is that due to the velocity pressure alone.

For the conditions outlined, the general flow equation may be simplified to

$$\frac{U^2}{2g} = -\Delta H \quad (7)$$

Since at the tube mouth the fluid velocity is practically zero, the upstream velocity is

$$U = \sqrt{2g\Delta H} \quad (8)$$

Adiabatic conditions have been assumed. Probably this is not strictly true, but the error so introduced is slight since when this device is used for flow measurements comparatively small differences in pressure are developed, especially if the fluid is a gas. Moreover, under such circumstances it is justifiable to assume that

$$U = \sqrt{2gV\Delta P} \quad (9)$$

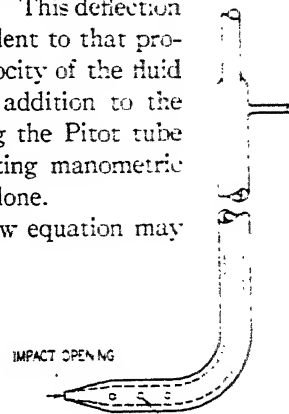


FIG. 4. Pitot tube.

By substituting for  $V\Delta P$  the "head,"  $h$ , expressed in feet of the fluid flowing, Equation 9 may be written

$$U = \sqrt{2gh} \quad (9a)$$

For Pitot tubes not correctly designed it may be necessary to multiply readings by an experimentally found correction constant. With  $U$ , the velocity of flow, the pipe size, and the fluid conditions known, it is a matter of arithmetic to calculate the quantity of fluid flowing in any specified time.

**Nozzles.** These are employed primarily for two purposes, to measure flow and to convert efficiently the energy of a flowing fluid to kinetic energy. The former use is exemplified in some industrial instruments, and the latter in the various rotating and stationary nozzles in steam turbines. In either, the thermodynamic analysis is much the same, although design details differ between the two.

**Fundamental Relations.** As nozzles are operated, the terms  $X$ ,  $Q$ , and  $W$  are either zero or negligible.

By a first law balance

$$\Delta \frac{U^2}{2} = -\Delta H$$

By a work balance

$$\Delta \frac{U^2}{2g} = - \int V dP - L$$

By a material balance

$$\frac{U_1 A_1}{V_1} = \frac{U_x A_x}{V_x}$$

**Actual Operation.** The condition of the fluid entering the nozzle is usually either completely determined or assumed. Often nothing more than the pressure is known at exit.

This makes necessary a solution based to a certain degree on empirical relations unless reversibility may be assumed. In practice, nozzles may be designed in which the actual velocity attained is 94–96 per cent of that reversibly possible.

When dealing with fluids condensable within the operating range of the nozzle, supersaturation may occur — the vapor although at temperatures less than saturation does not condense during its rapid passage through the nozzle. The causes for this and the empirical methods for correction will not be discussed in this book.

**Definitions.**

$$\text{Nozzle efficiency} = \frac{U_2^2 - U_1^2_{\text{actual}}}{U_2^2 - U_1^2_{\text{ideal}}} \quad (10)$$

$$\text{Coefficient of velocity} = \frac{U_{2\text{the}}}{U_{2\text{the}}} \quad (11)$$

**Some Characteristics of Fluid Flow Through Nozzles.** Whenever any fluid is allowed to flow through a nozzle, because of the three fundamental relations previously given there is, at every point, a necessary although often complex relation between the pressure and the specific volume of the fluid. Moreover, irreversibility is increased if at any section along the nozzle the area is not the correct size to accommodate the flowing fluid. If a plot is made of correct nozzle areas (at right angles to fluid flow) against pressures at various points along the nozzle, interesting results are obtained:

1. For *non-compressible fluids* it is found that the nozzle must be converging.

2. For *compressible fluids* it is found that the nozzle must be converging down to a certain pressure and at still lower pressures must become divergent. The exact nozzle form is a matter of experiment, but it is roughly as shown in Figure 5. The narrowest section is called the throat. Moreover, in nozzles with a convergent section only, if attempts

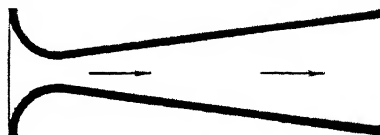


FIG. 5. Nozzle.

are made to increase the flow of a compressible fluid, by decreasing the pressure at the nozzle exit, entrance pressure remaining fixed, an exit pressure is reached below which additional decreases have no effect on the quantity of fluid passing. The quantity flowing becomes independent of the back pressure. This is called a critical flow pressure. (This critical pressure must not be confused with that previously mentioned in connection with  $P$ - $V$ - $T$  relations for gases.) The ratio of a critical flow pressure to its corresponding entrance pressure is called the critical flow pressure ratio. For a given fluid over not too widely different entrance conditions the critical flow pressure ratio is roughly independent of the entrance pressure. For air and steam it varies between 0.50 and 0.55. When a fluid has been expanded in a nozzle to its critical flow pressure it will be found to have attained a velocity equal to that of sound in the flowing fluid.

**Ideal Nozzle.** By assuming reversible adiabatic operation the velocity attained in a nozzle when operating between inlet pressure  $P_1$  and discharge pressure  $P_2$  may be calculated. For materials where

## FLUID FLOW

sufficient data are available, *i.e.*,  $T$ - $S$  or  $H$ - $S$  diagrams, a convenient expression is

$$\Delta \left( \frac{U^2}{2g} \right) = -\Delta H_{\text{rev.}}$$

If the gas laws may also be assumed,

$$\Delta \left( \frac{U^2}{2g} \right) = -\frac{kP_1 V_1}{k-1} \left[ \left( \frac{P_2}{P_1} \right)^{(k-1)/k} - 1 \right]$$

This together with the continuity equation makes possible calculation of nozzle areas at different points along the nozzle for any desired flow rate.

**Orifice.** An orifice is a constriction placed in a pipe. Since friction loss and mechanical difficulties are increased by making the constriction longer than necessary for mechanical strength, the orifice often takes the form of a plate perforated with a circular hole of the chosen size. Unlike the Pitot tube an orifice introduces considerable irreversibility (pressure drop). To minimize this as large a hole as is consistent with a satisfactory reading of the instrument is advised. Orifices vary in diameter from 30 to 80 per cent of that of the pipe.

As a fluid passes through an orifice, its velocity must increase owing to the smaller cross-sectional area for flow. An energy balance may be written between a section considerably upstream and that at the orifice.

$$Q - W = \Delta E + \Delta(PV) + \Delta X + \Delta \left( \frac{U^2}{2g} \right) \quad (14)$$

Here  $W$  and  $\Delta X$  are zero and  $Q$  is negligible. The resulting simplified equation is

$$\Delta \left( \frac{U^2}{2g} \right) = -\Delta H \quad (15)$$

This is a general equation for flow through an orifice. The available energy balance may also be made the basis for orifice calculations. For this

$$-\int V dP = \Delta \left( \frac{U^2}{2g} \right) + L$$

If *reversible adiabatic* conditions are assumed  $L = 0$  and  $\int V dP = \Delta H$ . The equation then becomes as before

$$\Delta \left( \frac{U^2}{2g} \right) = -\Delta H \quad (17)$$

**Vena Contracta.**<sup>1</sup> As the flowing fluid approaches the orifice, it is highly probable that parts originally near the retaining pipe will be gradually deflected towards the center that they may pass through the opening. Experiment indicates that this effect starts a short distance above the orifice and is not complete when the plate is reached. Contraction continues for a distance beyond this point, and then once more the flowing stream widens again to fill the pipe. The conditions may be much as indicated in Figure 6. The narrowest section of the flowing stream is called the *vena contracta*. The cross-hatched areas (Figure 6) represent fluid more or less stagnant as compared with the main stream. Owing to the flow action the more slowly moving fluid probably tends to assume roughly the shape required for a nozzle, although the downstream form is no doubt poorly defined. Some irreversibility probably occurs in this section as the rapidly flowing streams again fan out to fill the pipe.

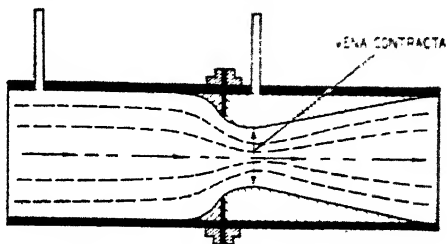


FIG. 6. Sharp-Edged Orifice

To indicate the pressures required, taps must be provided. One of these is preferably placed at an upstream point before that where stream contraction and resulting pressure drop occur. The second may be placed at the *vena contracta*. Often throat taps are used, the upstream being one pipe diameter above and the downstream one-third diameter below the orifice plate. Probably most common are flange taps where the pressure openings are in the flanges between which the orifice plate is clamped.

It is customary to use the actual orifice diameter in calculations of flow, but it is evident that the pressure corresponding is practically never known but rather that beyond, where additional contraction or re-expansion of the stream may have occurred. Moreover, flow is not strictly reversible. Neither of these shortcomings influences the basic relation

$$\Delta \left( \frac{U^2}{2g} \right) = -\Delta H$$

However, with only the pressures known, it is not possible to determine the enthalpy change for an irreversible adiabatic process, and even more serious, there is no simple method of getting the pressure at the orifice.

<sup>1</sup> In the free discharge of a liquid through an orifice the *vena contracta* is actually visible and measurable.

It is usual to calculate flow rate using the basic formula on the assumption that flow is reversible and that the downstream pressure is actually measured at the orifice plate. To compensate for the considerable error so introduced, the calculated flow rate is multiplied by an empirical constant, the *coefficient of discharge*. Values of this coefficient may range from 0.6 to 0.80 in commercial installations.

**Effect of Variable Stream Velocity.** Review of the description for either turbulent or viscous flow indicates that at no section is the velocity of the flowing fluid the same at all points across the pipe, although at the *vena contracta* uniform velocity does prevail across the flowing stream. The easiest method of circumventing this troublesome detail is to use the correctly averaged velocity at any section.

**Orifice Formulas for Non-Compressible Fluids.** The following expressions for use in orifice calculations are either evident or readily derived.

$$\frac{\text{Average velocity at section 1}}{\text{Average velocity at orifice}} = \frac{U_1}{U_0} = \frac{A_0}{A_1} \quad (18)$$

$$r r^2 - U_1^2 = - \quad (19)$$

$$U_0 = \frac{\sqrt{-2g\Delta H}}{\sqrt{1 - \left(\frac{A_0}{A_1}\right)^2}} \quad (20)$$

Since under the conditions here considered

$$\Delta H = V(P_0 - P_1) \text{ approximately} \quad (21)$$

$$U_0 = \frac{\sqrt{-2gV(P_0 - P_1)}}{\sqrt{1 - \left(\frac{A_0}{A_1}\right)^2}} \text{ approximately} \quad (22)$$

As previously indicated, because of the location of the manometer taps,  $P_0$  is usually not known but rather  $P_2$ , the pressure at a section somewhat downstream from the orifice. This and other minor discrepancies are allowed for by inserting a correction factor,  $C$ . Equation 22 then becomes

$$U_0 = \frac{C\sqrt{-2gV(P_2 - P_1)}}{\sqrt{1 - \left(\frac{A_0}{A_1}\right)^2}} \quad (22a)$$

**Orifice Formulas for Compressible Fluids.** If the pressure drop is but a few per cent of upstream pressure, the formulas of the preceding section are suitable for compressible fluids. For large pressure drops, however, recourse must be had to the general expression previously formulated,

$$\Delta \frac{U^2}{2} = -\Delta H \quad (23)$$

When it may be assumed that operation is reversible and adiabatic, the gas laws apply, and  $k$  is constant, the previous equation may be written

$$\Delta \frac{U^2}{2g} = \frac{kP_1 V_1}{(k-1)} \left[ 1 - \left( \frac{P_0}{P_1} \right)^{(k-1)/k} \right] \quad (23a)$$

If  $U_1$  may be neglected, the volume of fluid passing the orifice per second will be

$$A_0 \sqrt{\frac{2gkP_1 V_1}{k-1}} \left[ 1 - \left( \frac{P_0}{P_1} \right)^{(k-1)/k} \right] \quad (24)$$

Since in actual flow reversibility is not attained and since the pressure is measured at a section downstream from the orifice, a more useful expression is obtained by substituting for  $P_0$  the pressure measured,  $P_2$ . To offset this and departure from the assumed conditions the volume flowing is multiplied by a correction factor—the experimentally-determined orifice coefficient. The actual mass rate of flow then is

$$\frac{m}{\theta} = \frac{CA_0}{V_1} \sqrt{\frac{2gkP_1 V_1}{(k-1)}} \left[ 1 - \left( \frac{P_2}{P_1} \right)^{(k-1)/k} \right]$$

or

$$\frac{m}{\theta} = CA_0 \sqrt{\frac{2gkP_1}{(k-1)V_1}} \left[ \left( \frac{P_2}{P_1} \right)^{2/k} - \left( \frac{P_2}{P_1} \right)^{(k-1)/k} \right] \quad (24a)$$

If a plot is made of quantity of fluid passing the orifice versus  $P_2$ , according to the above equation the curve will pass through a maximum. The upstream pressure,  $P_1$ , is assumed constant. Actually the flow does increase with decreasing values of  $P_2$ , eventually reaching a constant volume beyond which further decrease of  $P_2$  has no influence. The phenomenon is similar to that noted in nozzles with high pressure drops.

**Venturi Meter.** This instrument for measuring fluid flow, Figure 7, is made up of a carefully constructed convergent entrance section followed by a well-designed divergent diffuser section. Pressure taps are attached at a point before convergence starts and at the narrowest

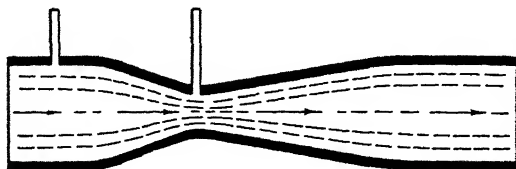


FIG. 7. Venturi Meter.

section, the throat. The purpose of the diffuser section is to restore the pressure to as near its value before the fluid entered the instrument as is possible. To this end the diffuser section is necessary even for small pressure drops between the gage taps. This is a sharp contrast to the requirements for divergent sections on nozzles.

Flow through a well-designed Venturi meter is 96 to 98 per cent of that given by reversible conditions. The fundamental relations are

$$\Delta \frac{U^2}{2g} = -\Delta H \quad \text{and} \quad \frac{U_1 A_1}{V_1} = \frac{U_x A_x}{V_x}$$

**Ejectors.** These are of increasing importance in engineering work, especially where large volumes of low-pressure vapors are to be compressed to moderate pressures or discharged to the atmosphere. Ejectors

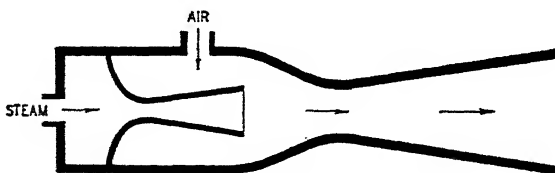


FIG. 8. Ejector (Diagrammatic).

tors consist of a *nozzle* (Figure 8) in which the *driving fluid*, usually steam, expands to give a high-velocity jet. This action reduces the pressure in the *mixing chamber* sufficiently to cause the *driven vapor* to be drawn in. Both vapor streams mingle and at the expense of the kinetic energy in the moving stream are compressed in the diffuser to the discard pressure. The operation is highly irreversible, and, although the general principles of fluid flow are applicable, usually insufficient data on discharge conditions are available to make exact calculations possible. Ejector design is largely empirical.



## SUMMARY

1. The importance of the three basic equations in fluid flow calculations was emphasized. For steady flow these are

$$\text{The first law equation: } Q - W = \Delta H + \Delta X + \Delta \left( \frac{U^2}{2g} \right)$$

$$\text{Bernoulli's theorem: } -W_{\text{shaft}} - \Delta(PV) - \Delta X - \Delta \left( \frac{U^2}{2g} \right) + \int P dV = L$$

$$\text{A material balance, the continuity equation: } \Delta \left( \frac{UA}{V} \right) = 0$$

2. The critical flow phenomenon for compressible fluids was described and the critical pressure ratio was defined as  $(P_1/P_{cf})$ , where  $P_1$  is the original pressure and  $P_{cf}$  the corresponding critical flow pressure.

3. The utility of the Pitot tube, the nozzle, the orifice, and the Venturi meter as instruments for measuring fluid flow was discussed. Relations of importance in calculations concerning these are:

$$\Delta \frac{U^2}{2g} = -\Delta H$$

$$\Delta \left( \frac{UA}{V} \right) = 0$$

## NOTATION FOR CHAPTER XI

*Upper Case:*

<i>A</i>	Cross-sectional area of conduit
<i>C</i>	Coefficient of discharge
<i>D</i>	Diameter, feet
<i>E</i>	Internal energy
<i>F</i>	Force acting to cause motion
<i>H</i>	Enthalpy
<i>L</i>	Lost available energy due to friction
<i>P</i>	Absolute pressure
<i>Q</i>	Heat withdrawn from surroundings (added to system)
<i>R</i>	Retarding frictional force
<i>U</i>	Velocity
<i>V</i>	Volume
<i>W</i>	Work done by system on surroundings
<i>X</i>	Height above datum

*Lower Case:*

<i>f</i>	Fanning friction factor (Figure 1)
<i>g</i>	Gravitational acceleration, 32.2 ft./sec. <sup>2</sup>
<i>h</i>	Fluid head (expressed as feet of the fluid flowing)
<i>k</i>	Ratio of $C_p$ to $C_v$

$l$	Length of pipe, Equations 5 and 6
$m$	Mass
$\frac{m}{\theta}$	Mass rate of flow, pounds per second
$y$	Length

*Subscripts:*

0	Refers to orifice
1, 2, $x$	Sections 1, 2 or $x$

*Greek Letters:*

$\Delta$	(Final value) — (Initial value)
$\theta$	Time (seconds)
$\rho$	Density
$\mu$	Viscosity, (lb.)/(sec.) (ft.)

## PROBLEMS

1. The following data were collected on a straight 2-in. pipe line carrying water at 70°F.

- Upstream pressure, 150 lb./sq. in. abs.
- Downstream pressure, 100 lb./sq. in. abs.
- Vertical elevation of inlet above outlet, 50 ft.
- Discharge, 800 gal./min.

What is the friction?

2. An elevated tank is to be erected to supply water at 50°F. to a cooling coil. It is necessary to have a pressure of 40 lb./sq. in. abs. at the coil inlet when delivering 100 gal./min. The line leading from the tank to the coil is standard 2-in. pipe free of bends and valves. At what minimum height above coil inlet must the bottom of the tank be?

3. A compressed-air line, used for removing the cake from a filter, is made up of 1½-in. pipe and has an equivalent length of 250 ft. This line must be capable of delivering 500 cu. ft. of free air (measured at 70°F.) per minute at a pressure of 4 atm. abs. What pressure must the pump delivering to the line be capable of maintaining, assuming that:

- (a) Flow is isothermal. (b) Flow is adiabatic.

In either case the air is delivered to the line from the pump at 90°F.

4. Water at 68°F. is flowing through the following measuring devices at a rate of 2.2 cu. ft./min. Calculate the reading expressed in inches of water which would be obtained on each.

- (a) A 1-in. orifice, in a 5-in. pipe ( $C = 0.60$ ).
- (b) A 1-in. Venturi in a 3-in. pipe ( $C = 0.98$ ).
- (c) A Pitot tube in the center of a 3-in. pipe. (Assume the average velocity is 0.80 that at the center.)

5. A standard 3-in. main delivering water to a cooler is provided with a sharp-edged orifice ( $C = 0.61$ ) having an opening 2 in. in diameter. The static pressure on the upstream side is 100 lb./sq. in. abs., and the temperature is 80°F. At full

capacity the orifice reading is found to be 1.5 in. of mercury, the manometer legs being full of water above the mercury. How many gallons per hour are passing through the pipe?

6. A long straight line (12 in. inside diameter) is to be provided with a sharp-edged orifice for measurement purposes. The line will carry air at about 1 atm.  $70^{\circ}\text{F}$ ., the air velocity ranging from 20 ft. to 80 ft. sec. A gage inclined 10 in. horizontal, to 1 in. vertical, using water as a liquid, will be used to record the static pressures on the two sides of the orifice. A scale is to be attached to the gage so that at a gas velocity of 50 ft./sec. a reading of 5 in. will be obtained. If the orifice coefficient is 0.70, what must be the diameter of the orifice?

7. A gas mixture containing 75 mol per cent hydrogen and 25 mol per cent nitrogen is passing through a 5-in. inside diameter straight steel pipe under a pressure of 25 atm. and  $70^{\circ}\text{F}$ . A Pitot tube placed in the center of the pipe shows a reading of 1 in. of water. Assuming that the average gas velocity is 0.85 that at the pipe center, how many pounds of gas per minute are passing through the pipe?

8. Air is flowing isothermally ( $60^{\circ}\text{F}$ .) at a constant rate of 0.030 lb. sec. through a horizontal pipe having an inside diameter of 2.07 in. The absolute pressure at the entrance to the pipe is 2 in. of mercury, and the pressure drop is 1 in. of mercury.

Calculate the friction and the heat loss from the pipe, both expressed in B.t.u. per second.

9. A supply of gasoline at  $68^{\circ}\text{F}$ . having a viscosity of 0.667 centipoise and a specific gravity of 0.76 is pumped through a 6-in. horizontal pipe at the rate of 500 gal./min. At the end of 200 ft., this pipe branches into three lines consisting of 3-, 2-, and 1-in. pipes, respectively. If these pipes have lengths of 700, 325, and 125 ft., respectively, and discharge at atmospheric pressure, what is the percentage of total flow through each one?

10. Phosgene gas is flowing at a pressure of 50 atm. abs. and a temperature of  $205^{\circ}\text{C}$ . into a 1-in. pipe, entering it at a linear velocity of 200 ft. sec. It leaves the pipe at 40 atm. abs. At this temperature the viscosity of phosgene gas may be assumed 0.02 centipoise. Granting isothermal flow and neglecting entrance and exit losses, calculate the friction loss through this pipe. The critical temperature of phosgene is  $182^{\circ}\text{C}$ ., and the critical pressure 56 atm. abs.

11. Tabulate the velocities which could be obtained by isentropic expansion of steam from 300 lb./sq. in. abs., and  $200^{\circ}\text{F}$ . superheat, to 200 lb. sq. in., 100 lb. sq. in., 75 lb./sq. in., 50 lb./sq. in., 25 lb./sq. in., 10 lb. sq. in., and 3 in. of mercury.

Tabulate the velocities which could be obtained by adiabatic expansions to these same pressures, if the efficiencies of the nozzles required for the expansion were 95 per cent for the three highest back pressures, and 90 per cent for the remainder.

12. Find the throat and exit diameters of the nozzles to be used in the isentropic expansions of Problem 11. In each case the nozzle is to handle 100 lb. of steam per hour.

## CHAPTER XII

### POWER CYCLES

**Introduction.** To illustrate the application of the two fundamental laws to actual processes of industrial importance, the next three chapters, predominantly descriptive, are included at this point. In some respects this is a digression from the previously followed plan, but in view of the importance of work generation this departure seems justifiable.

Although the sun is our most important and practically only source of energy, all attempts to utilize solar energy directly on a large scale for commercial production of work have failed. Results in a few experimental installations indicate a possibility of solving this problem, but for the present those great stores of sun energy, the fuels, must be used in the generation of work.

To produce work, so necessary for the continuance of our society, the stored energy must be released. So far but one important method has been developed for doing this. By a combustion process the energy is converted to heat and this in turn used to develop pressure in a working fluid. In some cases this pressure, working on pistons as in engines, brings about mechanical motion; in others the pressure is used to develop fluid velocity. The kinetic energy arising from this is then converted to mechanical energy by allowing the fluid to impinge on rotatable parts as in turbines.

These methods will be extremely inefficient unless strict observance to the inflexible rules resulting from the second law teaching is followed.

A greater part of the available energy stored in our fuels could well be converted to useful ends were it possible to develop work-production processes which would not include the step of first converting the stored energy to heat. If carbon-consuming batteries, so-called fuel cells, could be built, these might be operated at moderate temperature levels and yield work directly as electricity. Commercially, the numerous attempts to do this have failed. During the last thirty or forty years the major effort has been to improve the efficiency of our known and tried methods for generating power rather than to develop new ones. But this should not lead one to ignore the possibility of newer and better methods.<sup>1</sup>

<sup>1</sup> Internal combustion engine cycles will not be discussed. The chemical engineer seldom needs to consider them in detail.

**Practical Power Cycles.** In most industrially important power plants the working substance is passed through a closed cycle of processes. Equipment common to all such cycles includes a furnace, in which the stored fuel energy is released as heat; a pressure vessel, the boiler, which contains the working fluid and to which heat is transferred, causing vaporization; some type of prime mover (an engine or turbine) from which work may be taken; a condenser in which heat is discarded and the fluid once more converted to a liquid in preparation for its return to the boiler. The Carnot efficiency must give the limiting value for that fraction of the heat supplied which can be converted to work under ideal conditions.

**Rankine Cycle.** Early workers despaired of ever being able to construct an apparatus to operate on the Carnot cycle, and for engines, in which the working fluid suffers condensation during one step, they substituted the more easily realizable but still idealized Rankine cycle. Today this does not merit anything like the attention previously given it, although one cannot say that it has been entirely discarded.

The many interesting air or gas cycles containing no condensation step, proposed around the turn of the century, although now commercially obsolete, constitute an interesting phase of development. Of all, probably the Ericsson was the most important, and many hot-air engines were actually built. Reference to any of the older books devoted to mechanical engineering thermodynamics will yield descriptions of several. In spite of a high efficiency, their bulk and size, for a given power output, made them undesirable.

Figures 1 and 2, representing the Rankine cycle on the  $T$ - $S$  and  $H$ - $S$  planes, respectively, will be useful in describing the essential steps. In either figure  $a$ - $b$  is a reversible adiabatic expansion of vapor in an engine or turbine;  $b$ - $c$  is condensation of the vapor in a condenser;  $c$ - $d$  is a complex step consisting of pumping the fluid from the condenser to the boiler and heating to boiler temperature; the final step  $d$ - $a$  is evaporation at constant pressure to form the saturated vapor once more at condition  $a$ . Reference to Figure 1 clearly shows the inefficiency due to the step  $c$ - $d$ , wherein some of the heat is picked up at temperature levels below that of the highest temperature source available. In a Carnot

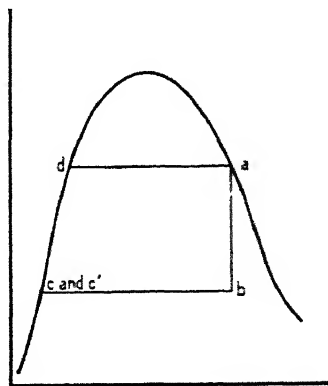


FIG. 1. Rankine Cycle on the  $T$ - $S$  Plane.

cycle all the heat absorbed would be received at the highest available temperature.

The work added by pumps in raising the water from condenser to boiler pressure is small and, if the pumping is assumed reversible and adiabatic, would show up as a very short vertical step on either diagram. It has been entirely neglected in Figure 1 and shown exaggerated as  $c-c'$  on Figure 2.

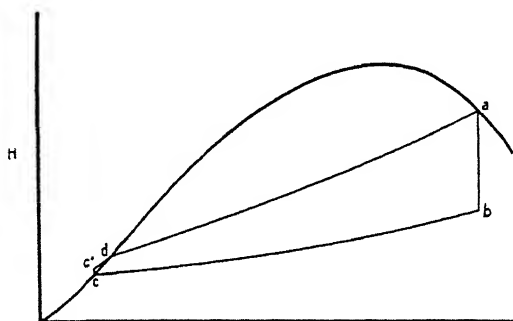


FIG. 2. Rankine Cycle on the  $H$ - $S$  Plane.

If pump work is neglected the Rankine cycle efficiency, ratio of work output to heat input, is

$$\frac{H_a - H_b}{H_a - H_c}$$

**Modern Power Cycles.** For highest efficiency it is necessary that all operations be carried out as near reversibly as possible. To this end various improvements over earlier procedures are common in present-day plants.

**Heat Absorption.** That this step may introduce but little inefficiency, it is necessary that the temperature difference between furnace and the working fluid in the boiler be a minimum. Even with modern equipment this temperature difference is considerable, but much improvement has been made by raising the operating temperature of the boiler. This is readily done in a steam boiler by raising the pressure. Operating pressure of 1500 to 2500 lb./sq. in. are not uncommon.

With increasing temperature, inefficiency due to the irreversible heating of the condensed fluid from condenser to boiler temperature becomes of considerable importance. This is true not only because the liquid line which represents practically the path followed departs from the vertical, but also because, as one moves towards the critical, the amount of heat to be absorbed during the desirable constant-temperature vaporization process diminishes, eventually becoming zero as the critical is

reached. To counteract these evils the use of regenerative feed heating and multiple fluid cycles is practiced. The latter is economical only in larger installations, and even the former is hardly worth while in small installations.

Superheating of the vapors, at practically constant pressure, is nearly always worth while. Here again inefficiency due to transferring heat at a temperature level less than the highest available is evident, but at least all heat is absorbed at temperatures higher than those for either fluid heating or vaporization.

Heat for superheating theoretically is more completely converted to work than that absorbed from the furnace during other parts of the cycle. Practically superheating often results in even greater increase in efficiency. A wet vapor gives rise to increased rate of heat transfer and to increased flow friction over that of a dry or superheated vapor. Both of these are sources of loss. Moreover, especially in turbines, wet steam often leads to serious erosion on blades and nozzles. All these are minimized by having the vapors sufficiently superheated so that, even after expansion, the moisture will not be excessive, 10–20 per cent.

**Action of Fluid in Engine or Turbine.** This phase has received a great amount of study, and the discussion associated with it is sufficiently important to merit a separate chapter, that on engines and turbines.

**Heat Rejection.** Modern efficient condensers, so located that the pressure drop between engine or turbine and condenser is a minimum, make heat rejection at low temperatures practical. Available cooling water determines an asymptotic level to which condensation temperature may approach. Usually in modern plants it is not considered economically sound to have the temperature difference between cooling water and condensing steam less than 10–20°F. It would seem that other parts of the cycle offered more chance for future developments than this.

**Regenerative Feed-water Heating.** When feed-water at condenser temperature is pumped directly into a boiler, mixing is highly irreversible. Especially in larger plants it is possible to do much towards eliminating this source of inefficiency. Theoretically the solution is easily seen — heat the water progressively with a series of heating media each but slightly higher in temperature than the water being heated. Practically the difficulty is to provide the series of heating fluids at the various temperatures. In either the older multiple expansion reciprocating steam engines or the newer so-called bleeder or extraction turbines, it is possible to withdraw steam at stages during expansion and obtain the desired sources of heat at a series of temperatures intermediate between those of condenser and boiler. Such steam streams, properly proportioned in amount, led back to a multiple-section feed-water heater, are

an essential part of the regenerative feed heating process, shown in Figure 3. The condensed steam and water heated in any stage leave as a common stream. This forms the liquid feed to be heated in the next stage. For ideal operation it is necessary that the amount of steam bled at each step be just sufficient so that the heated feed and the condensed steam may be at the same temperature as they mix.

Actually regenerative feed heating is usually not economically practical in small plants, and even in large installations the use of more than four stages is unusual. It is considered good practice to locate the

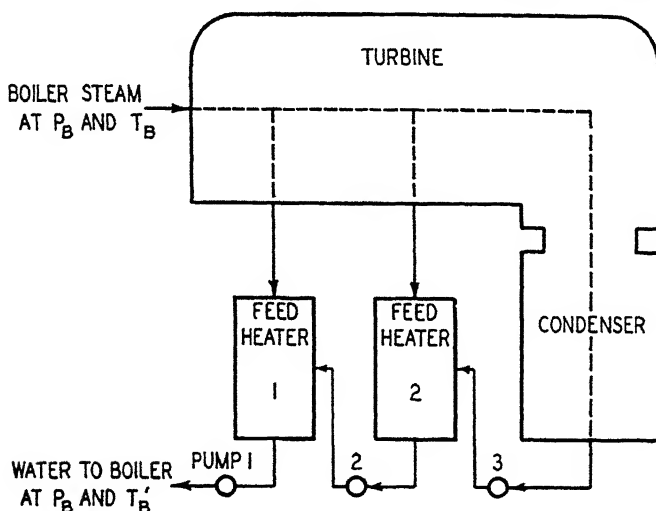


FIG. 3. Two-Stage Regenerative Feed-Water Heating Power Cycle.

extraction points so that as one passes from condenser to boiler through these points the corresponding saturated steam temperatures change by approximately equal increments.

**Multiple Fluid Cycles.** The use of increasing differences in temperature between boiler and condenser leads to the necessity for some method of minimizing the ever-increasing irreversibility encountered in heating the liquid. Regenerative feed-water heating is one method of combating this difficulty. Another solution to the problem would be to use a working fluid having a low liquid heat capacity and therefore a steeper liquid line as plotted on the  $T$ - $S$  plane. This results in less difference between the Carnot and Rankine efficiencies, both working between the same limits. A fluid with negligible liquid heat capacity would yield a vertical liquid line. But such is not available, and indeed for all liquids the heat capacity increases with temperature.



The idea of using one fluid over the range where its liquid heat capacity is favorable and at higher temperatures changing to a second fluid is promising. Moreover, the necessity for working with very high pressures at elevated temperatures may be avoided by a proper choice of the second fluid. A third advantage is gained in that the range over which the second fluid is used may be considerably below the critical condition where the "dome" on the  $T$ - $S$  diagram becomes narrow, *i.e.*, the enthalpy change on vaporization becomes small. Inefficiency due to a high liquid heat capacity plays a role of increasing importance with decreasing enthalpy of vaporization, as study of the Rankine diagram on the  $T$ - $S$  plane will show.

In the light of these evident advantages one would think that the use of multiple-fluid cycles would be widespread. This is not so. Probably no cycles using more than two fluids are in successful commercial operation, and the number of these now working is extremely limited.

Not only does the use of more than one fluid necessitate more complicated construction, but in addition the choice of suitable fluids other than water is narrow. When the imposing list of desirable characteristics

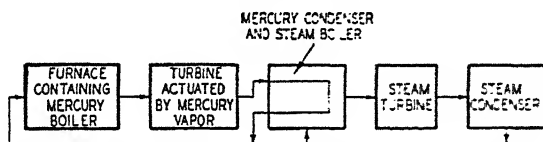


FIG. 4. Flow Diagram for a Mercury-Water Cycle.

such a fluid must possess is considered, this is not surprising. In addition to being chemically stable at the temperatures encountered it must be non-corrosive to the ordinary materials of construction, should have thermal properties desirable from the viewpoint previously mentioned, and for ease in handling should not solidify at the temperature of the surroundings. In addition it should be comparatively inexpensive and preferably non-poisonous in liquid and vapor form.

In spite of some of its shortcomings, mercury seems most desirable as a second fluid, and a few mercury-water cycles are in operation. A skeleton diagram for a mercury-water cycle is given in Figure 4. Owing to the low enthalpy of vaporization of mercury relative to water it is necessary to circulate about 9 lb. of mercury for each pound of water.

Among other second fluids which have received favorable consideration are diphenyl and diphenyl oxide. These have been employed to a limited extent as liquid heating media. For such uses the general thermodynamic considerations regarding efficiency when using fluids in power cycles are pertinent. Before turbines and water condensing equipment had been developed to their present

high efficiency there was a limited use of sulfur dioxide as a secondary fluid to decrease the lower operating temperature, water serving as the primary high-temperature fluid.

**Reheating Cycles.** The inefficiency of heating the cold feed with fluid at boiler temperatures was decreased by a stepwise heating using steam which had been lowered in temperature by allowing it to do work. In somewhat the same manner the advantages of superheating may be enhanced by a process of resuperheating. To this end the steam after

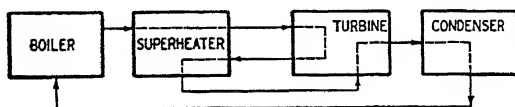


FIG. 5. Flow Diagram for a Reheating Cycle.

passing part way through the turbine is withdrawn and returned to be reheated, approximately to its original temperature, but, since no pump is used in this step, at a lower pressure.

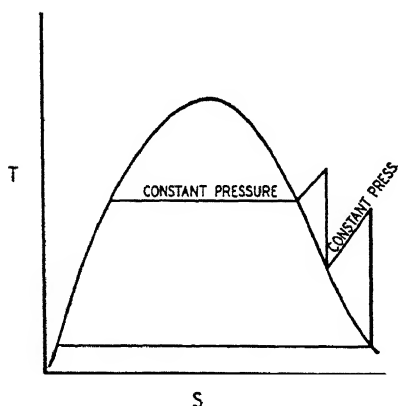


FIG. 6. The Reheating Cycle on the  $T$ - $S$  Plane.

The difficulty and inefficiency of returning the large volume of vapor corresponding to low pressures leads to the conclusion that this process will be most advantageous in high-pressure plants, where, even after partial expansion, the specific volume of the steam is still relatively small. From an operating viewpoint reheating is often desirable because it serves to prevent excess moisture formation in engines and turbines working over wide pressure ranges.

A flow diagram of the process is given in Figure 5; Figure 6 is a somewhat idealized analysis of the reheating step on the  $T$ - $S$  plane.

**Cycle Efficiencies.** It is desirable to have some method of comparing the efficiencies of the various cycles relative to one another. Since of all possible heat engine cycles, operating between two temperature levels, the Carnot is the most efficient, the ratio of the efficiency of any cycle to that of the Carnot, operated between the same two temperature extremes, might be taken as a figure of merit for evaluation purposes. This is often done.

Perhaps a more interesting comparison is the ratio of work output to the available energy originally supplied to the cycle. Such a measure of efficiency is not only in strict accordance with the second law principle but also of universal applicability, even serving for operations such as rectification, distillation, and analogous processes. In these, where the desired output is not directly energy as work, the increase in availability of the substances being transformed is to be used in the numerator rather than the work output as suggested for power cycles.

Since the available energy input to any operative power cycle is the free energy of the fuel measured above a datum of surrounding conditions, the overall cycle efficiency may be stated as:

$$\text{Efficiency} = \frac{\text{Work output}}{\text{Free energy input}}$$

This method of expressing efficiency takes cognizance of any shortcomings in furnace operation as well as losses in the associated equipment. Moreover, it provides a satisfactory basis for judging possible future developments in work generation such as fuel cells.

**Value of Steam.** Often, especially in chemical industries, steam is used not only to actuate work-generating equipment, such as turbines and engines, but in addition to supply heat (work-producing ability) for process work. To proportion properly the cost for steam which first passes through work-generating equipment on its way to process apparatus is an involved problem to which no universally applicable answer can be given. However, from a strictly thermodynamic viewpoint such steam is of value in direct proportion to the amount of work capacity it has relative to what it originally had.

### SUMMARY

Various industrially important power cycles have been considered including such modifications as regenerative feed heating, multiple fluid operation, and resuperheating. These, as well as the general tendency to ever higher fluid temperatures and lowest economically attainable condenser temperatures, are but applications of the second law teaching.

A suggested method of determining the thermodynamic efficiency of any process or cycle is

$$\text{Efficiency} = \frac{\text{Energy available as work in output}}{\text{Energy available as work in input}}$$

The possibility of evaluating steam in a strictly thermodynamic sense is presented in terms of the above method of expressing efficiency:

$$\frac{\text{Present value of steam}}{\text{Original value of steam}} = \frac{\text{Present availability}}{\text{Original availability}}$$

## PROBLEMS

1. Draw the Carnot cycle on the  $T$ - $S$  diagram, and show how the heat absorbed, the heat rejected, and the work done are represented on the diagram. Discuss, with reference to the  $T$ - $S$  diagram for steam, the use of this fluid as the working substance in an engine.

2. Experimental engines have been built using hot water as a working fluid. In such engines no vaporization occurs. With water at 500 lb./sq. in. abs. and 467°F. and heat rejection at a constant temperature of 100°F., what is the maximum work-producing capacity per pound of hot water fed to the engine?

3. Estimate the thermal efficiencies (work output divided by heat input) of the following power cycles:

- (a) Carnot cycle receiving heat at 444.59°F. and discarding it at 100°F.
- (b) Rankine cycle, using steam, receiving heat at 444.59°F. and 400 lb./sq. in. abs.; constant condenser temperature 100°F.
- (c) Rankine cycle, using steam, with boiler at 400 lb./sq. in. abs. generating steam superheated 120°F.; constant condenser temperature 100°F.

4. A chemical plant, requiring process steam at several different pressures, obtains power from a bleeder turbine installation. The turbine operates essentially isentropically and is supplied with steam at 500 lb./sq. in. abs. superheated 250°F. Steam may be bled off at 300 lb., 100 lb., 50 lb., 30 lb., 25 lb., and 10 lb. Estimate the charge which should be made to the various departments using process steam, basing your calculations on the value of a pound of bled steam at the various extraction pressures and expressing the cost relative to boiler steam.

Had steam at the various pressures been obtained by direct throttling of boiler steam, what would have been the value of the steam so obtained relative to the value of boiler steam?

5. A waste heat boiler generates 20,000 lb./hr. of steam at 70 lb./sq. in. abs., and 180° superheat. The plant requires 10,000 lb./hr. of dry saturated process steam at 18 lb./sq. in. abs. It is proposed that the high-pressure steam be expanded down to 18 lb./sq. in. in a turbine and the desired process steam be drawn off, whereupon the remaining steam is to be sent back to the boiler to be heated to 421°F. and then put through a lower-pressure turbine exhausting at 4 lb./sq. in. abs. One stage of regenerative feed heating is to be employed, the steam for this purpose being bled off, just after leaving the high-pressure turbine. The make-up water for the boiler, plus any additional water required, will be used as cooling water in the condenser, and it will be assumed for purposes of preliminary design that the cooling water will leave the condenser at the same temperature as the condensate.

1. Calculate: (a) the pounds of steam used for the regenerative feed heating per pound of steam generated in the boiler; (b) the work done per pound of steam generated.

2. Criticize the above proposed installation.

6. Estimate the efficiency of a mercury-steam power plant, operating on the conventional Rankine cycle (saturated vapor for both fluids), in which the mercury is evaporated at 100 lb./sq. in. abs. and condensed at 2 lb./sq. in. abs., a 20°F. temperature difference being allowed in the mercury condenser. The steam is condensed at 100°F. What is the ratio of the efficiency of this plant to that of a Carnot cycle between the same extreme temperature limits? How many pounds each of mercury and of steam must be circulated, neglecting heat losses, per 1000 kw-hr. produced,

if the turbines and generators are ideally efficient (*i.e.*, no mechanical or electrical losses)?

The specific heat of liquid mercury is 0.1375, 0.1377, and 0.1388 joule per gram at 100, 200, and 280°C., respectively ("International Critical Tables," Vol. 5, p. 113). The vapor pressure of mercury is given by the formula:

$$\log_{10} p = \frac{-52.23 \times 58.7}{T} + 7.752 \quad (\text{"International Critical Tables," Vol. 3, p. 206})$$

where  $p$  is in millimeters of mercury and  $T$  is in degrees K. What would be the efficiency of the plant if two stages of regenerative feed heating were used in the steam cycle: bleeding boiler steam for the first stage, and withdrawing wet steam at 70 lb./sq. in. abs. from the turbine for the second stage? In this case, the remainder of the steam at 70 lbs./sq. in. abs. will be returned to the boiler room and superheated 50°F. before being introduced into the low-pressure turbine stages.

7. A bleeder-type turbine takes steam at 200 lb./sq. in. abs. and superheated 150°F. and exhausts to a condenser at 2 in. of mercury abs. The condensate flows through two feed-water heaters and back to the boiler. The feed-water heaters are supplied with steam bled from the turbines at 60 lb. sq. in. abs. and 7 lb. sq. in. abs. In each heater the condensed bleed-off steam flows out with the heater water. Assuming expansion in the turbine to be isentropic, the liquid water fed to each heater to be at the saturation temperature corresponding to the pressure in the previous unit, and the fluid leaving each heater to be liquid water at the temperature corresponding to saturation at the pressure in the heater, calculate, per pound of steam fed to the turbine:

- (a) The pounds of steam bled off to each heater.
- (b) The work output of the turbine.
- (c) Heat supplied in the boiler and superheater.
- (d) Thermal efficiency of the cycle.
- (e) Pounds of steam to the turbine per horsepower-hour output.

Compare your answers to parts (b) to (e), inclusive, with the corresponding values for a Rankine cycle working between the same supply and exhaust conditions.

## CHAPTER XIII

### STEAM ENGINES AND TURBINES

Of the various units comprising a steam power plant, probably the prime mover, engine or turbine, has undergone the most intensive development. As a result such difficulties as mechanical friction and leakage of steam from one part to another have been largely eliminated.

To minimize thermodynamic shortcomings has required, in addition to consideration of mechanical details, clear insight into the fundamental principles. The two main sources of inefficiency in engines and turbines were, and to a certain extent still are:

- (1) Undesired heat flow with consequent loss in available energy.
- (2) Fluid friction, primarily Joule-Thomson effects with attendant irreversibility and decreased work capacity.

**Fundamental Considerations.** In the thermodynamic analysis of either engine or turbine operation the first and second law principles are utilized in a somewhat restricted sense.

Since overall potential and kinetic energy effects are of minor importance in a well-designed unit, the energy balance for steady flow conditions in this case reduces to

$$Q - W_{\text{shaft}} = \Delta H$$

Where heat losses are small, as is usual in turbines (but not necessarily in engines), this is further simplified to

$$-W_{\text{shaft}} = \Delta H$$

Owing to absence of any form of chemical reaction, analysis according to the second law, although somewhat complicated, is facilitated. This is accomplished by a study of the individual factors contributing to irreversibility. As is so frequently true, these are best evaluated in terms of available energy changes. Since the processes of interest here are, for the most part, those approximating reversible adiabatic conditions, the use of the entropy concept is especially convenient, although interpretation in terms of availability is widespread among modern workers.

Turbines are preferred for power generation, but in many chemical operations considerable quantities of low-pressure steam are required in addition to power. Often a small reciprocating steam engine offers an

efficient and reliable means for obtaining the necessary process steam and, at small cost, the required power.

### STEAM ENGINES

**Reciprocating Engines.** Although the general idea of a steam turbine preceded that of the engine, the engine reached a considerable state of development long before the turbine attained any commercial importance.

Fundamentally all reciprocating engines consist of one or more cylinders fitted with pistons. Each cylinder is provided with one or several openings for inlet and exhaust of steam. Most cylinders are double acting, steam being admitted on both sides of the piston. With this arrangement about twice as much power is obtained from a cylinder as would be obtained from a single-acting arrangement. Unlike most gas compressors, where the valves are operated by a difference in gas pressure on the two valve sides, engine valves are positively and definitely operated, often by a mechanical linkage controlled by cams or eccentrics attached to the engine shaft. This assembly, the valve gear, is built in a great many different forms and has been the object of far-reaching mechanical development as it was the source of considerable inefficiency in earlier engines. The gear must be so constructed that the valves, especially those controlling steam admission, open and close as quickly as possible since during these operations they exert a throttling effect, usually spoken of as "wire drawing," on the steam passing. This fluid friction is distinctly irreversible.

The Corliss oscillating valve actuated at the proper time by a vacuum cylinder, the dash pot, enjoyed a long period of popularity but could not operate satisfactorily at speeds of more than a few hundred cycles per minute. Today the poppet valve common to most automobile-type internal-combustion engines is in widespread use. Small simple engines still have some type of sliding valve such as the D valve (so named because of its shape). Locomotive engines frequently employ a piston valve, probably because of simplicity and reliability.

**Cylinder Processes.** As steam is admitted to the engine cylinder the piston moves out and eventually a point is reached where the inlet valve closes. This point is called **cutoff**. The steam, enclosed in the cylinder, now expands, in the ideal case reversibly and adiabatically, doing work on the piston at the expense of the fluid's internal energy. Near the end of piston travel, irrespective of the condition of the expanding steam, the exhaust valve opens. This point is known as **release**. If the steam is above exhaust pipe pressure at this point, it blows out of the cylinder irreversibly until practically exhaust pressure is reached.

The piston starts back towards its original position and expels from the cylinder additional steam, eventually reaching a point near the end of its return stroke where the exhaust valve closes, **compression**, locking in the cylinder a quantity of steam at exhaust line pressure. Kinetic energy stored in the moving parts continues piston motion to the end of its stroke, compressing the steam already in the cylinder. Compression of the steam serves as a method for stopping and reversing the fast-

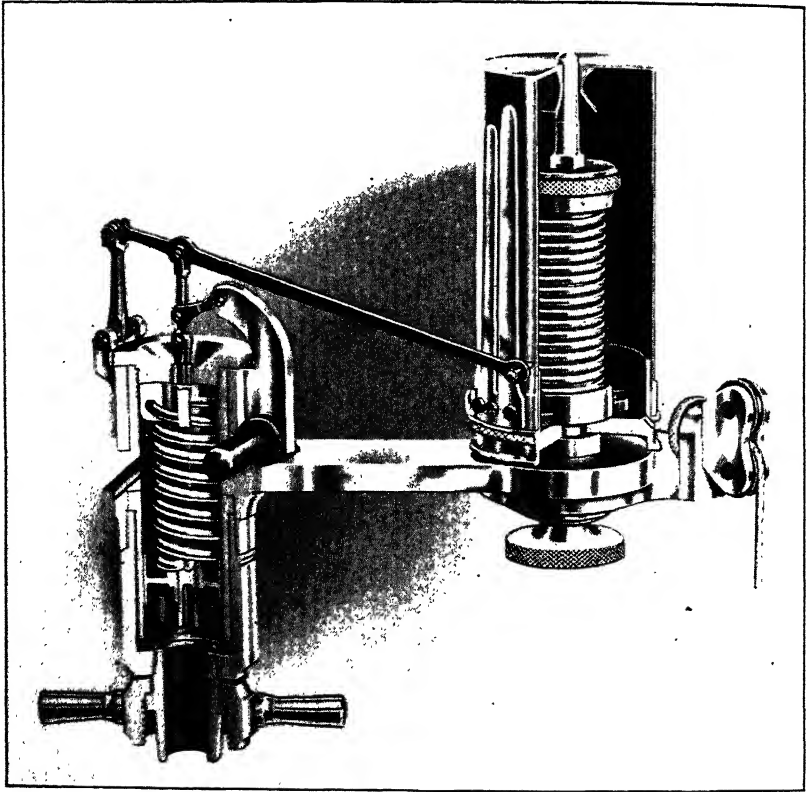


FIG. 1. Steam-Engine Indicator (Courtesy Crosby Steam Gage and Valve Co., Boston).

moving piston. Moreover, clearance between piston and cylinder head when the piston is at the end of its stroke is necessary to prevent mechanical interference between the two as the inevitable expansions and contractions due to temperature changes occur. At the end of compression the inlet valve opens. This point, **admission**, marks the entrance of additional steam to the cylinder. A complete cycle of cylinder processes has now been outlined.



**Indicators.** To aid in analyzing the processes occurring in the cylinder it is customary to follow the  $P$ - $V$  history of the steam under change. This is readily done by steam engine indicators. These were introduced by Watt, who constructed the engine indicator as a means for measuring experimentally the pressure-volume relations in the cylinder of an engine.

An indicator (Figure 1) consists of a small auxiliary cylinder fitted with a piston, one end of which is connected to the cylinder space of the engine to be tested. The instrument piston rests against a calibrated spring, deflection of which is recorded on a paper card. The card is automatically moved mechanically in a direction at right angles to that of the pressure indications by an amount proportional to the displacement of the engine piston. Since the volume change in the fluid in the engine cylinder is proportional to the movement of its piston, the instrument draws a diagram showing the  $P$ - $V$  relations of the fluid.

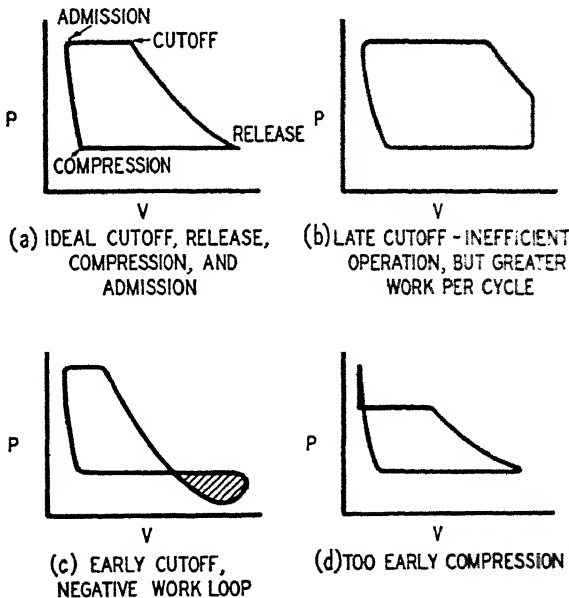


FIG. 2. Engine Indicator Cards.

to scales, the origin and the axes of which are determined by the adjustment of the instrument. Indicators are widely used in following performance characteristics of piston-in-cylinder machines.

**Indicated Work.** Measurement of the indicator card area, usually by planimetering, gives directly the information required for calculating work done on the engine piston, often called the indicated work. This is possible because the instrument is so designed and operated that ordinates on the card are directly

proportional to pressures in the engine cylinder, abscissas being proportional to piston displacements.

Moreover, the indicated work may be thought of as given by a rectangular area, the length of which is volume swept by the piston,  $LA$ , and the height a pressure such that

$$\text{Indicated work per power stroke} = PLA$$

This averaged pressure is called the *mean effective pressure* (M.E.P.). If  $N$  is the power strokes made by the engine in a minute,

$$\text{Indicated horsepower} = \frac{PLAN}{33,000}$$

**Valve Adjustment.** A second useful purpose served by the indicator is that of detecting and aiding in correcting improper valve settings. Figure 2 illustrates diagrammatically several possible cards.

**Engine Governing.** By valve adjustment the relative times at which the different cylinder events occur may be changed, and often an engine is governed by automatically controlling the point of cutoff in accordance with the power requirements placed on the engine. This is far more efficient than merely controlling the amount of steam admitted by manipulating a pressure valve in the steam line. Partly opening such a valve, as would be necessary at low engine loads, would cause marked irreversibility due to throttling the steam passing to the engine. Except where efficiency is subordinate, throttle governing is not used.

**Inefficiency due to Heat Flow.** Whenever steam in the cylinder is at a different temperature from the metal with which it is in contact, heat flow will occur. Losses from this source are increased if either or both steam and walls are wet, since the presence of moisture increases the heat-transfer coefficient. But as the steam expands, it does drop in temperature, and, if expansion is carried far enough, moisture will form. To reduce losses due to heat transfer the following expedients may be adopted:

1. Especially on larger units, jacket the cylinders with boiler steam. This is but a partial solution as losses occur owing to heat transfer from the jacket to the cooler steam during the latter parts of the expansion stroke, the exhaust stroke, and the earlier part of the compression stroke.

2. When operating over wide pressure ranges, use multiple cylinders, expanding over a part of the range in the first and over successive ranges in succeeding ones — *compounding*. This makes for complication and expense of construction but does decrease the temperature variation in any one cylinder. It also makes possible both the use of

small parts at the high-pressure end with consequent decreased expense of construction and in addition lowered losses because of smaller areas for heat transfer.

3. Use separate sets of valves for cold exhaust and hot inlet steam. This is common practice where efficiency is of major importance.

4. Utilize the uniflow principle as indicated in Figure 3. This type of engine has efficient poppet inlet valves mechanically controlled from the crankshaft and a central set of exhaust ports which are

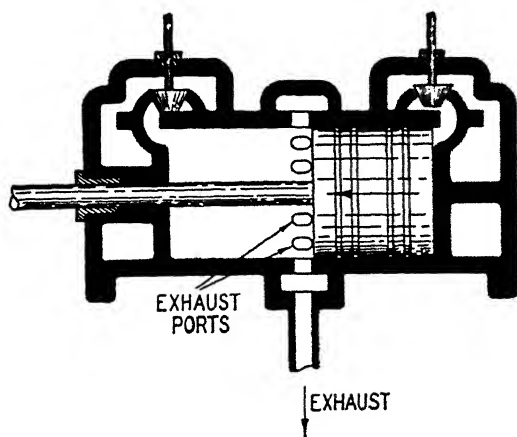


FIG. 3. Diagrammatic Cross-Section of Uniflow Engine Cylinder.  
(Note exhaust ports midway in cylinder and thick piston.)

uncovered by the piston. By such a construction the cold expanded steam is not passed back along the cylinder walls to valves located in the cylinder head with attendant loss, but instead flows always unidirectionally through the engine. Control of the point where compression starts is lost in uniflow engines, and sometimes auxiliary exhaust valves operated by pressure difference between cylinder and exhaust line are installed at an appropriate location in the cylinder wall.

**Use of Diagrams for Engine Analysis.** The  $T$ - $S$  and  $H$ - $S$  diagrams are widely used in thermodynamic analysis of engine operation. The path in an ideal reversible engine may be represented by a single vertical line on either plane. To follow the exact path taken by the fluid in an engine working with more than ideal cutoff (incomplete expansion) is a task of some complexity. Figure 4 on the  $T$ - $S$  has been drawn to indicate, by the shaded area, the loss in available energy due to incomplete expansion, all other processes considered ideal.

For actual operation, the  $T$ - $S$  path is likely to be somewhat as indicated in Figure 5. Here again the shaded area represents the loss in available energy due to irreversible effects.

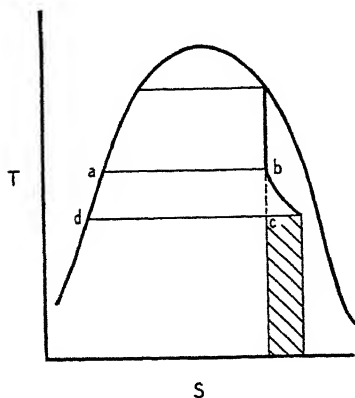


FIG. 4. Idealized Steam Engine Operation on the  $T$ - $S$  Diagram. (Incomplete Expansion.)

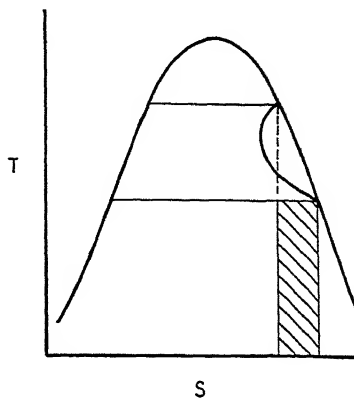


FIG. 5. Actual Steam Engine Operation on the  $T$ - $S$  Diagram.

**Shortcomings of Reciprocating Engines.** The difficulties of designing reciprocating engines to work efficiently over the wide pressures and temperature limits of modern power plants were never completely eliminated. Especially troublesome was the question of handling, without serious pressure drop, the very large volumes of steam when working with modern efficient condensing equipment. Even with large exhaust valves, drop between the low-pressure cylinder and the condenser was likely to be serious. In spite of their low upkeep cost and ability to carry widely fluctuating loads or even heavy overloads with comparatively high efficiency, where power generation is of primary importance, engines have been largely displaced by turbines.

## TURBINES

Although for large power outputs turbines are much lighter and smaller than engines of similar capacity, they are not so efficient under widely ranging load conditions and, unlike reciprocating engines, will not carry heavy overloads.

**Turbine Types.** Fundamentally every turbine is so constructed that the expansion of steam serves continuously to turn a rotor, from which work may be taken.

There are two important types, the impulse turbine and the reaction.

Theoretically, for *impulse* action, the steam is expanded in stationary nozzles and the kinetic energy so acquired is utilized to turn the rotor by direction of the rapidly moving fluid stream against carefully designed blades or buckets arranged around the periphery of the rotating member. For true impulse action no expansion of steam occurs in the moving blades.

In *reaction* operation the machine is constructed with nozzles for steam expansion on the periphery of the rotor and steam inlet passages on the surrounding stationary parts. All expansion of steam should occur in the moving nozzles. Actually no practical turbine is wholly of the reaction type, and any machine in which pressure drop occurs across both stationary and moving blades is usually called a reaction turbine.

**Turbine Staging.** Early impulse turbines had but one set of rotating blades, and even with moderate pressure drops through the nozzles the steam attained extremely high velocities. It was only at excessive rotational speeds that efficient utilization of the kinetic energy in the fast-moving fluid could be realized. Attempts to pass the steam through the rotating blades once and then redirect it against the blades a second or third time, re-entry turbines, were not particularly successful in any but the smaller sizes. This difficulty led to the development of staged turbines. In *impulse pressure staging* the steam is expanded a moderate amount, passed through a set of rotating blades, and so on through many such steps. In this way efficient operation at moderate rotating speeds is possible. A reaction turbine with pressure staging is similarly arranged with the expansion nozzles rotating and the directive steam passages stationary.

*Velocity staging* is also practiced. In this several sets of rotating blades are arranged with redirecting passages between each set and the next. The steam passes through a set of nozzles and acquires a considerable kinetic energy. This is absorbed progressively as the fast-moving stream passes through the various sets of rotating blades, it being directed to each succeeding set by the stationary passages between. No expansion is supposed to occur in the passages.

Many modern turbines are a combination of impulse and reaction with both pressure and velocity staging.

**Extraction or Bleeder Turbines.** In these, provision is made to withdraw steam at one or more points part way through the machine. This arrangement is often particularly convenient in chemical industries where large or variable amounts of reduced-pressure process steam may be required. Extraction is usually to be preferred over direct throttling of boiler steam to process pressure levels.

**Definitions of Some Common Terms.** In connection with turbine design several terms are in general use.

The blade speed ratio =  $\frac{\text{blade } U}{\text{jet } U}$  where  $U$  = linear velocity.

The diagram efficiency applied to a single row of blades preceded by a nozzle is really that fraction of the total jet energy which may be expected to be converted to rotation energy in the blades. On the basis of certain simplifying assumptions and with a vector diagram, it is possible to calculate this efficiency. It is a useful indication of the probable actual performance of the blades. The connection

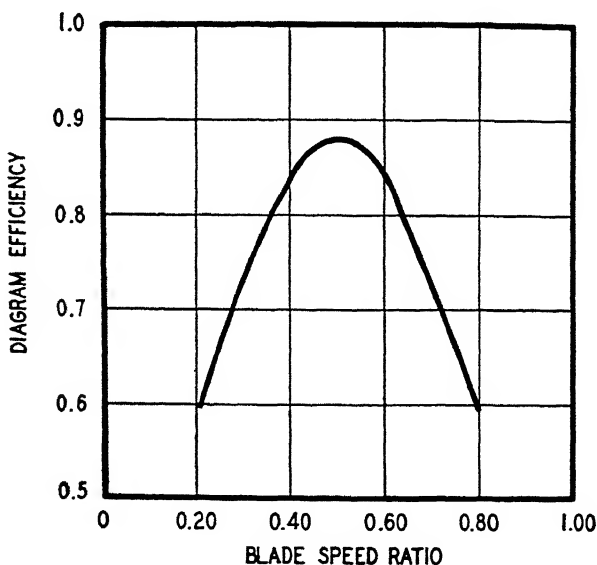


FIG. 6. Blade Speed Ratio and Diagram Efficiency.

between diagram efficiency and blade speed ratio is shown roughly by Figure 6.<sup>1</sup> This figure is enlightening as an aid in comparing the actual operating characteristics of turbines with those of reciprocating engines.

**Cumulative enthalpy drop** is a summation of the available enthalpy drops in the various stages with the assumption that not only is expansion isentropic but also that each expansion starts with steam at actual stage entrance conditions. This may be clarified by reference to Figure 7, an

<sup>1</sup> Based on Figure 92 of Kiefer and Stuart's "Thermodynamics," p. 363, New York, John Wiley & Sons, 1930.

$H$ - $S$  diagram representative of the action in an impulse turbine with five pressure stages. Here the cumulative enthalpy drop is the sum of the enthalpy drops represented by the four vertical dotted lines.

**Reheat factor** is the ratio of the cumulative enthalpy drop to the enthalpy drop resulting from isentropic expansion between initial and final pressures.

The **condition curve** is a smooth curve on the  $H$ - $S$  diagram drawn

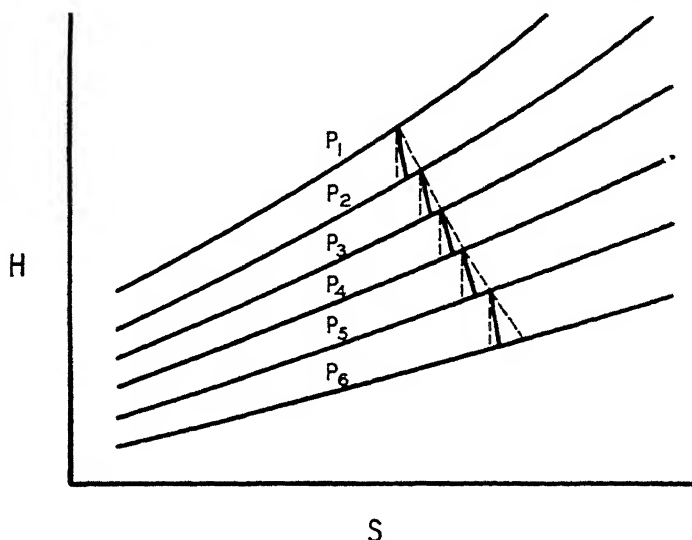


FIG. 7.  $H$ - $S$  Diagram for Impulse Turbine with Five Pressure Stages.

through the points representing the actual final states of the steam in the various stages. This is represented by the dotted curve of Figure 7.

**Turbine efficiency** is defined as actual work output divided by isentropic enthalpy drop both taken between the specified initial and final pressures. If entrance and exit velocities are neglected and there is no heat loss the efficiency is also the actual enthalpy change divided by the ideal isentropic change.

#### NOTATION FOR CHAPTER XIII

##### *Upper Case:*

- $A$  Area of piston
- $H$  Enthalpy
- $L$  Length of power stroke
- $N$  Number of power strokes
- $P$  Pressure; mean effective pressure

$Q$	Heat added to system
$S$	Entropy
$T$	Absolute temperature
$U$	Velocity
$V$	Volume
$W_{\text{shaft}}$	Shaft or flow work

### PROBLEMS

1. Derive a formula, in terms of quantities easily obtained from the steam tables for the work per cycle of a simple, adiabatic, single-acting steam engine with clearance. Assume reversible operation except for the necessary irreversibility introduced by incomplete expansion. Use as a basis of computation 1 lb. of steam admitted per cycle.

2. A simple single-acting steam engine, with negligible clearance operating reversibly except for the necessary incomplete expansion in some cases, and adiabatically, is supplied with steam at 120 lb./sq. in. abs., superheated 90°F. Exhaust is to the atmosphere, at 15 lb./sq. in. abs. Make a plot of steam consumption expressed as pounds of steam per horsepower-hour versus cutoff in percentage of stroke.

3. A steam engine is controlled by a simple throttle valve. When it is operating at reduced load, it is found that the steam, originally at 175 lb./sq. in. abs. and 100° superheat, must be throttled to 90 lb./sq. in. abs. What is the condition of the steam on the downstream side of the throttle valve? Assuming exhaust to the atmosphere and engine operation adiabatic and reversible, what is the maximum work per pound of steam available:

- (a) If steam at full line pressure is used?
- (b) If throttling to 90 lb./sq. in. abs. is practiced?
- (c) What is the ratio of the power output per stroke in the two cases, clearance neglected?

4. A simple steam engine, having negligible clearance, operating adiabatically and with negligible mechanical valve and port friction, is completely expanding steam from an absolute pressure of 150 lb./sq. in. and 500° superheat to 50 lb./sq. in. abs. Assuming the cutoff to be changed so as to admit 20 per cent less steam per stroke, no other change being made in engine operation, by what percentage is the indicated horsepower reduced? By what percentage is the indicated horsepower per pound of steam reduced? Assuming that, instead of reducing the power output by changing the cutoff, the valve action had been kept unchanged, but the steam had been throttled adiabatically from 150 lb. down to 130 lb. before it entered the cylinder, by how much would the indicated horsepower of the engine have been reduced? By how much would the horsepower-hours per pound of steam consumed have been reduced?

5. Show that the work obtained from a reversible, adiabatic engine or turbine is always numerically equal to the change in availability,  $\Delta B = \Delta H - T_0 \Delta S$ , for the change which the working substance undergoes in passing through the engine ( $T_0$  is the sink temperature at which heat is rejected).

6. A triple-expansion single-acting steam engine with negligible clearance is supplied with steam at 120 lb./sq. in. abs. superheated 90°F. The exhaust pressures of the three stages are respectively 65, 33, and 15 lb./sq. in. abs. Operation is reversible



and adiabatic in every way except that, in each cylinder, cutoff is so adjusted that expansion is only 80 per cent complete (as measured by the volume change in expansion) at the time when the exhaust valve opens. Calculate:

1. The dimensions of each cylinder, if 0.2 lb. steam per stroke are used and if stroke/diameter = 1 for the high-pressure cylinder.
2. The pounds of steam required per horsepower-hour delivered.

7. A uniflow steam engine, working reversibly and adiabatically, with cutoff such that the steam is expanded just to the back pressure, is supplied with steam at 180 lb./sq. in. abs. superheated 100°F. Calculate the steam consumption per hour of the engine provided that exhaust is at 10 lb., sq. in. abs.

8. A uniflow steam engine with an 8-in. bore and a 12-in. stroke is supplied with dry saturated steam at 200 lb./sq. in. abs. pressure. Exhaust is at 10 lb. sq. in. abs. Assuming reversible adiabatic operation and 5 per cent clearance, make a plot of steam consumption versus cutoff.

9. A direct-acting steam pump with negligible clearance takes steam at 300 lb. sq. in. abs. pressure, 100° superheated, and exhausts at 30 lb. sq. in. abs. Assuming adiabatic, frictionless operation of the pump, what is the condition of the exhaust steam?

10. A bleeder turbine takes steam at 200 lb./sq. in. abs. and 600°F. Exhaust is to a condenser at 2 in. of mercury abs. Steam may be bled off for process work at 30 lb./sq. in. abs. During normal operation the steam bled off amounts to 25 per cent of that supplied to the turbine. To the point of bleed-off the overall efficiency of the turbine is 70 per cent, while the efficiency from bleed-off to exhaust is 65 per cent. Assuming adiabatic operation throughout and negligible bearing friction, calculate:

- (a) The steam rate during normal operation in pounds per horsepower-hour.
- (b) The steam rate with no steam bled off.
- (c) The ratio of steam consumption during normal operation to that of operation where all process steam is obtained by throttling boiler steam to 30 lb. sq. in. abs.; all steam supplied to the turbine being expanded to 2 in. of mercury abs. and the efficiencies of the turbine being as above stated.

## CHAPTER XIV

### REFRIGERATION

Refrigeration machines, the primary purpose of which is the absorption of heat at one temperature level and its rejection at a higher, find ever-increasing application for the preservation of foods during storage and transport. In addition, refrigeration is utilized for such varied uses as control of chemical reaction, by keeping the reactants at reduced temperature, as is practiced in some of the acid treating processes used in the manufacture of gasoline; separation of wax from lubricating oils by a combined chilling and final centrifuging; separation by distillation of normally gaseous mixtures, as is done in the production of oxygen and nitrogen from liquefied air. Moreover, all truly complete methods of air-conditioning involve some type of refrigeration step.

A study of the many and varied arrangements for producing lowered temperatures, though they differ widely in detail, leads to the conclusion that thermodynamically all are fundamentally similar. The general principles previously formulated for changes in which energy plays a part must be applicable here.

In several respects refrigerators may be thought of as heat pumps. As a direct consequence of the second law, all require some form of work input or its equivalent. In contrast, heat engines produce work by absorbing heat at high temperature levels and rejecting it in part at low temperatures.

Industrially, it is often necessary to hold some material at a low temperature for certain steps in a manufacturing process but eventually to bring it back to the temperature of the surroundings. The separation of air into oxygen and nitrogen by the usual liquefaction methods is typical. In these procedures, owing to the relatively high cost of operating refrigeration processes, extreme care must be exercised to guard against irreversibility. One important safeguard against this is efficient countercurrent cooling of the reactants against the cold resultants. Although usually when working at higher temperatures, as in power-plant condensers, reduction of temperature differences between hot and cold streams to less than  $10^{\circ}$  or  $20^{\circ}$  is not considered economical, in gas liquefaction processes differences of a few degrees are not uncommon.

**Fundamentals.** If a refrigerator is thought of as a heat pump, for reversible operation the minimum work input is that necessary to reject the desired amount of heat of low-temperature origin to the surroundings

at the prevailing high temperature. This work must be numerically equal to that produced if the high-level rejected heat is allowed to return reversibly to the low-level source.

For reversible cyclical operation where all heat is absorbed isothermally at the lower level  $T_2$  and rejected isothermally at  $T_1$ ,<sup>1</sup> analysis of the energy relations by means of the  $T$ - $S$  diagram, Figure 1, shows that:

$$\frac{\text{Heat absorbed at } T_2}{\text{Heat rejected at } T_1} = \frac{T_2}{T_1}$$

Of more interest than this ratio, however, is that giving the ratio of heat absorbed, the really useful effect, to work required. Since  $Q_1 - Q_2 = W$ , it follows that

$$\frac{\text{Heat absorbed}}{\text{Work required}} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$$

The similarity between these ratios and those derived in connection with the Carnot power cycle is evident. A heat pump or refrigerator as above described is sometimes said to operate on a reversed Carnot cycle. A little thought shows that this gives for fixed lower and higher temperatures the minimum work requirement for the refrigeration effect,  $Q_2$ , obtained irrespective of the kind and arrangement of equipment used. Where variable absorption or discard temperatures are encountered the methods mentioned for treating the analogous situations in generalized reversible cycles are applicable.

**Thermodynamic Efficiency of Refrigerating Processes.** Certainly the most fundamental and probably the most satisfactory method of comparing refrigerating mechanisms on a basis of efficiency alone is that depending on work requirement. For any ideal process the increase in availability,  $\Delta B_1$ , due to discharging energy as heat from a low-temperature source to a high must be exactly equal to the decrease in availability,  $\Delta B_2$ , of the energy supplied to the mechanism. The thermodynamic efficiency of a refrigerator is then  $\Delta B_1/\Delta B_2$  — an expression equivalent to that used for the true thermodynamic efficiency of any process.

<sup>1</sup> Previously, heat absorbed from the surroundings has been given a positive sign. Here, because of common practice in engineering work, either heat absorbed or heat rejected will be considered positive in sign.

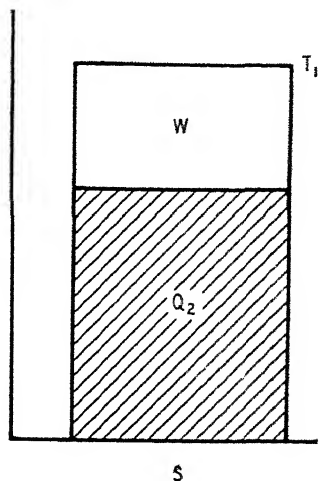


FIG. 1.  $T$ - $S$  Diagram for Reversible Refrigerating Cycle.

**Definitions of Terms.** Engineers have adopted the ratio of (Heat removed at  $T_2$ )/(Work required) as a measure of performance for refrigerating equipment. This is known as the *coefficient of performance*. To specify refrigerator capacity the "ton" is in common use. A machine having a capacity of 1 ton has a heat-absorbing capacity, per 24 hours of operation, equal to that of 1 ton of ice melted over the same time interval. Since the heat of fusion of ice is a function of temperature, a *standard ton* machine, by definition, is one which absorbs heat at a rate of 200 B.t.u./min.

It is interesting to note that a knowledge of both coefficient of performance and capacity is not sufficient to judge a machine properly unless, in addition, the operating temperature levels are known.

**Refrigeration Cycles. Compression Cycles.** Vapor compression cycles either with or without condensation of the compressed vapor are by far the most frequently used in modern machines.

For larger installations ammonia is the refrigerant generally used; for small units, sulfur dioxide or one of the newer halogen derivatives of the lower paraffin

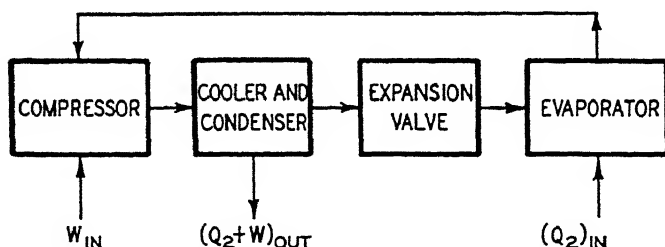


FIG. 2. Flow Diagram for Vapor Compression Cycle. (With Condensation.)

hydrocarbons. In addition the lower hydrocarbons such as propane and butane, or chlorinated hydrocarbon derivatives including methyl chloride, have at one time or another been used commercially. For installations where a leak is especially hazardous and in confined areas, as on boats, carbon dioxide or even air is not uncommon. A considerable amount of cooling, especially on trains and in industrial operations where the lower temperature is somewhat above 32°F., is accomplished by evaporation of water, using a steam jet ejector to furnish the required diminished pressure for evaporation.

A flow diagram of a vapor compression cycle with condensation is given in Figure 2; an idealized cycle of operation on the  $T$ - $S$  plane is shown in Figure 3.

Actual departure from the theoretical operation above presented is mainly due to non-ideal compression and expansion with resulting decreased coefficient of performance.

## ABSORPTION CYCLES

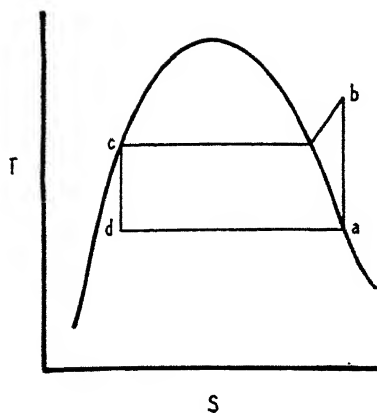


FIG. 3.  $T$ - $S$  Diagram for Vapor Compression Cycle.

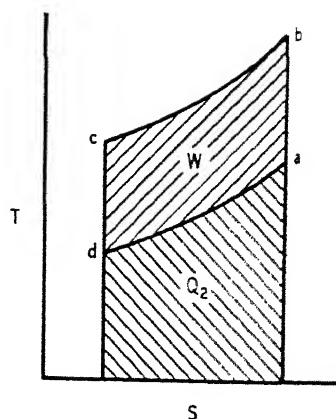


FIG. 4. Idealized  $T$ - $S$  Diagram for Compression Refrigerator. Without Condensation.,

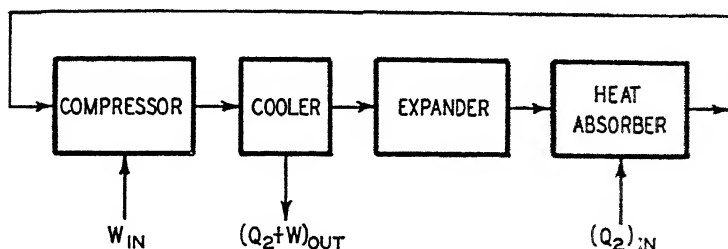


FIG. 5. Flow Diagram for Compression Cycle. Without Condensation.

An idealized cycle on the  $T$ - $S$  plane and the corresponding flow diagram are given in Figures 4 and 5 for a compression cycle in which condensation does not occur.

The expander is often an engine from which a portion of work may be obtained to aid in driving the compressor. Often, however, it is economically expedient to waste the work from the expander in some type of brake. Unless a carefully dried gas is used, difficulty with ice formation, especially in the valves, is likely.

**Absorption Cycles.** For operation on the absorption principle a suitable arrangement of apparatus is indicated in a flow diagram, Figure 6.

To draw the actual cycle on the  $T$ - $S$  or  $H$ - $S$  planes is not so easy as for the compression cycles. In general the use of an availability analy-

sis not only on the plant as a whole but in addition on each piece of equipment is a more satisfactory procedure.

Absorption cycles are characterized by the substitution of a generator and absorber with no moving parts, as a method of adding work capacity to the system, for the more simple compressor with its several moving parts and the necessary motor or engine to drive it.

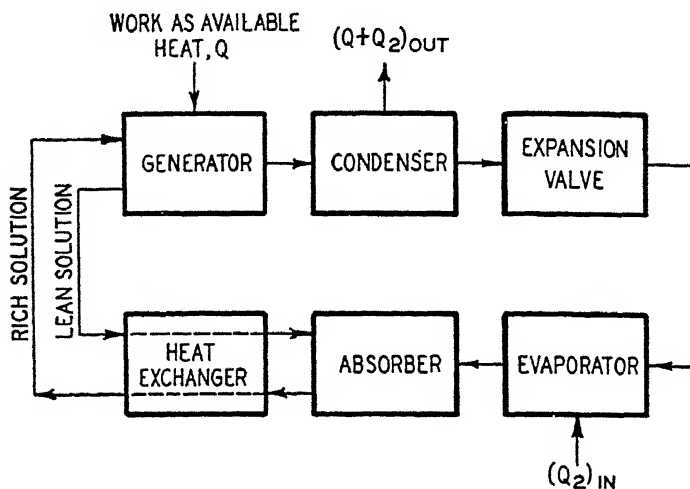


FIG. 6. Flow Diagram for Absorption Refrigerator.

**Jet Refrigeration.** This method is often used where but moderate drop in temperature is desired. Typical are those systems employing steam-actuated ejectors which cause evaporation of water, with resulting cooling effect, by lowering the total pressure over the water.

**Warming Engines.** An interesting application of the principles discussed in this chapter was proposed by Lord Kelvin many years ago. Known as the Kelvin warming engine, it is merely a refrigerating mechanism so arranged that in cold weather the outdoor surroundings serve as a source from which the machine takes heat and by the addition of work discharges it to the structure to be heated. Provided that the two temperatures are not too far apart this offers the possibility of utilizing one energy unit as work to discharge several units as heat. For cooling purposes the operation may be reversed but the intriguingly high theoretical coefficient of performance of the warming engine is no longer possible. Where climatic conditions are favorable, a few such installations have been built.

## SUMMARY

For any ideal cyclical refrigerator, operating between but two temperature levels, the ratio of heat absorbed at the lower temperature to work supplied is given by the expression:

$$\frac{Q_2}{W} = \frac{T_2}{T_1 - T_2}$$

By definition the coefficient of performance is:

$$\frac{\text{Heat absorbed at lower temperature}}{\text{Work input}}$$

By definition a ton of refrigerative capacity is equivalent to a heat absorption of 200 B.t.u./min.

On the basis of their operating cycles most refrigerators may be classified as either compression or absorption machines.

## PROBLEMS

- Using the following data, construct a  $T$ - $S$  chart for  $\text{SO}_2$ .

PROPERTIES OF  $\text{SO}_2$ 

("Refrigerating Data Book," 1939-1940)

## SATURATED SULFUR DIOXIDE

Temp.	Pressure lb./sq. in.	Vol. of Vapor cu. ft./lb.	Liquid Density lb./cu. ft.	Enthalpy of Liquid B.t.u./lb.	Enthalpy of Vapor B.t.u./lb.
-40	3.136	22.42	95.79	0.00	178.61
0	10.35	7.280	92.42	12.44	183.07
10	13.42	5.682	91.58	15.80	183
20	17.18	4.487	90.71	19.20	184
40	27.10	2.887	88.81	26.12	185
60	40.93	1.926	86.95	33.10	185
80	59.68	1.321	85.03	40.05	185
100	84.52	0.9262	83.07	46.90	184

## SUPERHEATED SULFUR DIOXIDE

Temp. °F.	Pressure (Sat. Temp.)	Volume cu. ft./lb.	Enthalpy B.t.u./lb.
20	10	7.939	186.7
	(-1.34°)		
	15	5.192	185.4
40	(14.43°)		
	10	8.316	190.1
	(-1.34°)		
	15	5.470	189.2
	(14.43°)		
	20	4.035	187.8
	(26.44°)		
	25	3.181	186.1
	(36.33°)		

## SUPERHEATED SULFUR DIOXIDE

Temp. °F.	Pressure (Sat. Temp.)	Volume cu. ft./lb	Enthalpy B.t.u./lb.
60	10	8.681	193.5
	(-1.34°)		
	15	5.734	192.8
	(14.43°)		
	20	4.251	191.8
	(26.44°)		
	25	3.363	190.6
	(36.33°)		
80	10	9.038	196.9
	(-1.34°)		
	15	5.988	196.4
	(14.43°)		
	20	4.454	195.6
	(26.44°)		
	25	3.536	194.7
	(36.33°)		
100	10	9.389	200.3
	(-1.34°)		
	20	4.648	199.3
	(26.44°)		
	50	1.650	193.9
	(70.40°)		
	70	1.181	187.6
	(88.97°)		

2. A refrigerating plant cycling 15 lb. of  $\text{SO}_2$  per minute abstracts heat from brine cooling coils at  $10^\circ\text{F.}$  and uses atmospheric air as a cooling medium in the  $\text{SO}_2$  condenser. Expansion is through a throttle valve. Compression may be assumed adiabatic and reversible. Plot against air temperature:

1. The refrigerative capacity of the plant expressed in tons.
2. The coefficient of performance.
3. The coefficient of performance assuming the throttle valve replaced by an expansion engine operating adiabatically and reversibly, and supplying part of the power required for compression.

3. A refrigerator using  $\text{SO}_2$  maintains a temperature of  $-10^\circ\text{F.}$  in the cooling coils. Cooling water at  $50^\circ\text{F.}$  is available. The liquid  $\text{SO}_2$  at  $60^\circ\text{F.}$  is passed through an expansion valve into the refrigerator coil.

(a) Per ton of refrigeration produced, estimate approximately how many pounds of  $\text{SO}_2$  must be cycled per hour.

(b) How much would the  $\text{SO}_2$  handled be reduced, provided that a reversible adiabatic engine could be used instead of the expansion valve?

(c) On the assumption that by countercurrent heat exchange against the vapor at  $-10^\circ\text{F.}$  the liquid  $\text{SO}_2$  could be cooled from  $60^\circ\text{F.}$  to  $-10^\circ\text{F.}$ , by how much would the  $\text{SO}_2$  handled be reduced?

(d) What percentage of the original liquid evaporates in (a), (b), and (c)?

4. List with reasons what you consider the important properties to be desired, from a thermodynamic viewpoint, in a refrigerant for use in a practicable vapor compression refrigeration system.

Such properties as non-toxicity, lack of odor, cheapness, and moderate vapor pressure at operating temperatures are important practically, rather than thermodynamically, and should be excluded from the answer to this question.



5. In a refrigerator, liquid  $\text{SO}_2$  at  $80^\circ\text{F}$ . is expanded through a reducing valve into the refrigerating coils where a pressure of 8 lb. sq. in. abs. is held, the  $\text{SO}_2$  vapor leaving these coils dry and saturated. A careful test shows an absorption of heat in the coils equal to 138 B.t.u./lb. of  $\text{SO}_2$  circulated. Is the performance equal to the ideal for this type of operation under these conditions? If not, to what may the departure from ideal be attributed?

6. An absorption-type refrigerator using an aqueous solution of ammonia is to be substituted for the unit mentioned in Problem 3, the lower temperature still being  $-10^\circ\text{F}$ ., the cooling water being at  $50^\circ\text{F}$ . If operation could be made reversible, how many pounds of ammonia would be cycled per ton of refrigeration produced. If dry steam at 100 lb./sq. in. abs. were available to operate this unit, how many pounds of steam would be consumed per ton of refrigeration?

## CHAPTER XV

### FUGACITY AND ACTIVITY<sup>1</sup>

**Introduction.** In this chapter two additional thermodynamic functions, fugacity and activity, are introduced. Both are merely aids to calculation and interpretation. Early experimenters developed a series of relations such as the gas laws, the laws of perfect solutions, and the law of mass action. These were originally empirical generalizations for the results of experiments performed, in many cases, over limited ranges. Such simple expressions offer the advantage that they are easily handled mathematically, but the disadvantage that they are not of general applicability. Certainly the gas laws cannot be used except at conditions far removed from the critical. Attempts to use the law of mass action, expressing concentrations in any of the usual ways, leads to error in almost all cases except those at high dilution.

There are at least two solutions to the problem here outlined. First, the old familiar expressions such as the gas laws, the laws of perfect solutions, and the mass action expression may be retained unchanged in form, except that, in place of pressures and concentrations, new variables may be substituted, so adjusted that over all ranges the correct thermodynamic result is given. Secondly, in place of the older, simple relations, more complicated equations may be set up which yield the correct result over all ranges, pressures, and concentrations being used as variables. Either suggestion leads to certain difficulties, but the first is the one usually followed by modern workers. The task is somewhat simplified because the new functions are chosen primarily to give results for the very important reversible isothermal changes rather than for all types of change. In this respect the functions to be discussed are of somewhat limited utility. Mathematically, they are intensive variables, point functions, and offer the advantages previously pointed out for such.

**Fugacity.** Often the determination of free energy changes is an important step in the analysis of engineering problems. For isothermal reversible changes involving simple compressions and expansions, in the

<sup>1</sup> Many of the ideas presented in this chapter were first developed and clearly enunciated by G. N. Lewis.

absence of chemical reaction,<sup>1</sup>

$$= \int V dP \quad (1)$$

If, in addition, the gas laws may be assumed applicable

$$\Delta F = NRT \ln \frac{P_2}{P_1} \quad (2)$$

The simplicity and ease of evaluating the free energy change when Equation 2 may be applied is evident. To retain these valuable features where the gas laws cannot be applied, a new function, the fugacity,<sup>2</sup> will be introduced. This is to be so chosen that for any process at constant temperature the free energy change of each substance or constituent taking part is

$$\Delta F_a = NRT \ln \frac{f_2}{f_1} \quad (3)$$

In Equation 3,  $f_2$  and  $f_1$  are the fugacities of substance  $a$  in its final and initial states, both being at the same temperature. In a given state the free energy of a particular substance is

$$F_a = N[RT \ln f + C_T] \quad 4$$

where  $C_T$  is a constant at any temperature. Moreover,

$$dF_a = NRT d \ln f \quad 5$$

Study of the above equations will show that, although for any substance the ratio of fugacities in any two chosen states is determined, the value of a single fugacity is not. Thus in Equation 3 the same result is given for  $\Delta F_a$  when  $f_2/f_1 = b_2/b_1$  as is given when  $f_2/f_1 = 2b_2/2b_1$  or any multiple of  $b_2/b_1$ . For a vapor following the gas laws

$$\Delta F_a = NRT \ln \frac{f_2}{f_1} = NRT \ln \frac{P_2}{P_1} \quad 6$$

Consequently it is convenient to choose the fugacity so that in the gas law range it will be equal to the pressure.

Although fugacity is often referred to as a corrected pressure, this may be misleading. In general, it is a function such that, first:

$$\Delta F_a = NRT \ln \frac{f_2}{f_1}$$

and second:

$$\text{Limit } \frac{f_a}{P_a} = 1$$

<sup>1</sup> Throughout the chapter, velocity and potential energy effects have been neglected.

<sup>2</sup> Lewis, *Proc. Am. Acad.*, 37, 49 (1901).

Essentially  $f_a = P_a$  over ranges where the gas laws hold. A careful consideration of these two facts indicates that fugacity is a corrective function applied over a range of values rather than at a single point.<sup>1</sup>

**Evaluation of Fugacity for Gaseous Systems.** Provided that the pressure-volume path is known to values such that the gas laws apply,

$$\int_{P_1}^{P_2} V dP = NRT \ln \frac{f_2}{f_1} = NRT \ln \frac{P_2}{P_1} \quad (7)$$

Solution of Equation 7 usually involves graphical integration. Use of the methods proposed in Chapter VIII may be helpful in approximating pressure-volume values for mixtures if, as is usual, experimental data are lacking. The evaluation may be expedited by expressing the molal volume,  $V_M$ , at any  $P$  and  $T$  by the equation

$$V_M = \frac{RT}{P} - r \quad (8)$$

where  $r$  is a correction term applied to the calculated gas volume  $RT/P$ . Since

$$RT d \ln f = V_M dP$$

and

$$V_M dP = \left( \frac{RT}{P} \right) dP - r dP$$

Then

$$RT d \ln f = \left( \frac{RT}{P} \right) dP - r dP$$

or

$$RT \ln \frac{f}{P} = - \int_0^P r dP \quad (9)$$

By plotting  $r$  against  $P$ , the value of  $f$  at any chosen value of  $P$  is readily obtained.

<sup>1</sup> For isothermal reversible flow processes where only mechanical effects are to be considered, it will be evident that

$$\Delta F = -W_{\text{net}} = NRT \ln \frac{f_2}{f_1}$$

Here the use of fugacity allows for any intake and expulsion work effects.

A detailed discussion of the fugacities of components of mixtures or other complexes will be postponed until a later chapter (Chapter XVIII).

**Calculation of Fugacity from  $\mu$ -Charts.** A little thought will show that for all gases following the  $\mu$ -charts it is possible to construct a *single* fugacity plot. Remembering that

$$NRT \, d \ln f = V \, dP$$

and

$$PV = \mu NRT$$

then

$$RT \, d \ln f = \left( \frac{\mu RT}{P} \right) dP$$

$$d \ln f = \mu \frac{dP}{P} \quad (10)$$

To avoid mathematical difficulties in evaluating  $f$ , write

$$\begin{aligned} d \ln f &= \left[ 1 - (1 - \mu) \right] \frac{dP}{P} \\ &= d \ln P - (1 - \mu) \frac{dP}{P} \end{aligned}$$

$$d \ln \frac{f}{P} = - \left( \frac{1 - \mu}{P} \right) dP$$

$$\int_1^{f,P} d \ln \frac{f}{P} = - \int_0^P \left( \frac{1 - \mu}{P} \right) dP$$

When  $P = 0$ ,  $(1 - \mu)/P$  is, for the particular value of  $T_R$  in question, the slope as read from the  $\mu$ -chart for a value of  $P = 0$ .

Thus:

$$\ln \frac{f}{P} = - \int_0^P \left( \frac{1 - \mu}{P} \right) dP \quad (11)$$

or in reduced quantities

$$\ln \frac{f}{P} = - \int_0^{P_R} \left( \frac{1 - \mu}{P_R} \right) dP_R \quad (12)$$

A glance at the  $\mu$ -charts shows that, at constant  $T_R$ ,  $\mu$  is a function of  $P_R$  only, and therefore at any temperature  $f/P$  must be a function of  $P_R$

only. The *solid lines* on Figure 1 have been constructed by evaluating the ratio  $f/P$  using Equation 12 and the  $\mu$ -charts. Figure 2 is an inter-

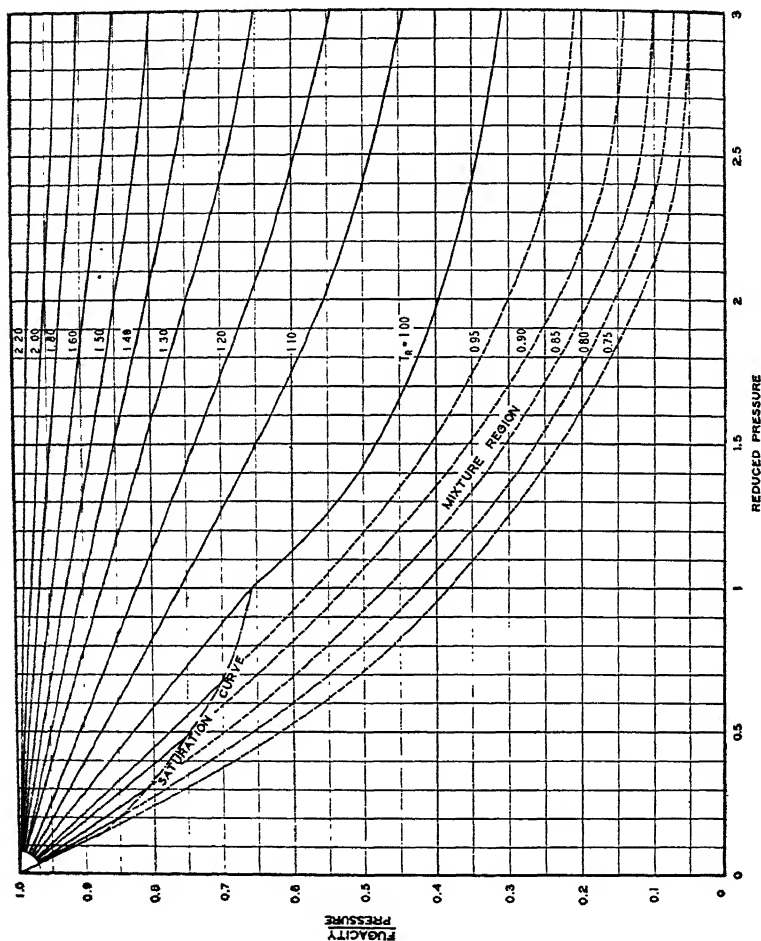


FIG. 1. Fugacity Chart. The Saturation Curve is Based on Paraffin Hydrocarbons.

mediate-range fugacity chart, and Figure 3 a high-range, both based on values by Newton.<sup>1</sup>

Different substances should be represented by different lines on these figures. At any reduced temperature, for similar types of materials, these lines fall in a comparatively narrow band. The bands of the various groups of materials are for simplicity represented by a single line.

<sup>1</sup> *Ind. Eng. Chem.*, 27, 302 (1935).

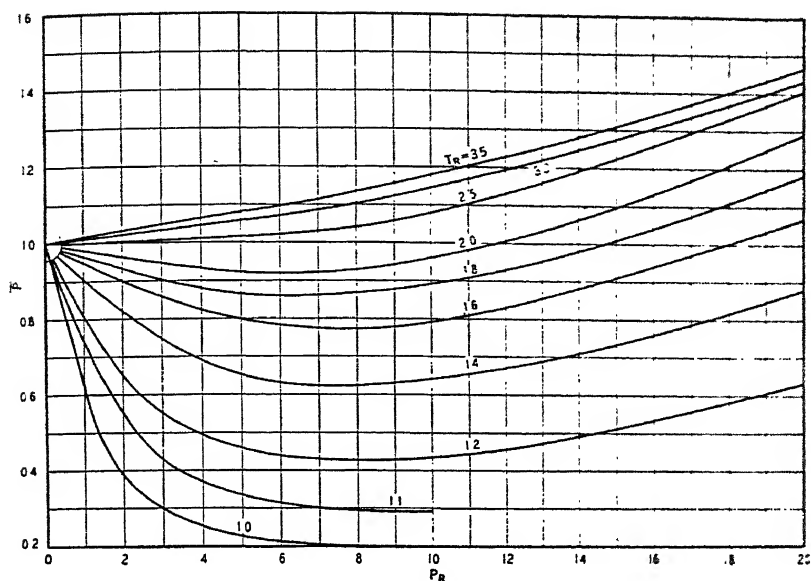


FIG. 2. Fugacity Chart for Intermediate Pressures and Temperatures.

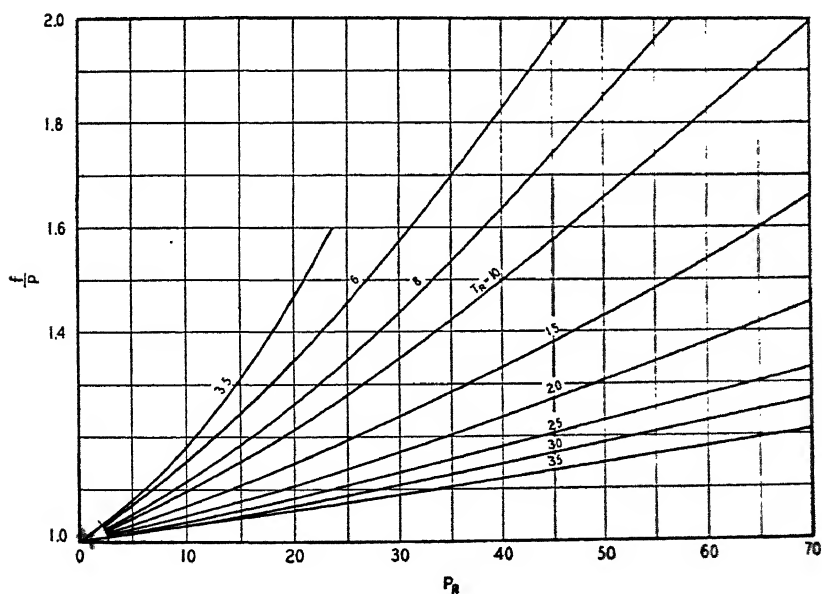


FIG. 3. Fugacity Chart for High Pressures and Temperatures.

If the assumption be made that a plot of  $\mu$  versus  $P$  for any substance at a fixed temperature yields, *over a short range*, a straight line passing through  $\mu = 1$  and  $P = 0$ , an interesting approximation previously pointed out by Lewis and Randall<sup>1</sup> may be derived. With this limitation  $-[(1 - \mu)/P]$  (Equation 11) is the slope of the line and therefore constant.

$$\ln \frac{f}{P} = \int_0^P C dP = CP$$

$$\frac{f}{P} = e^{CP} = e^{-(1-\mu)}$$

But when  $z$  is small,  $e^{-z} = 1 - z$

$$\frac{f}{P} = \frac{PV_M}{RT}$$

and since  $RT/V_M = P^*$ , the pressure according to the perfect gas law.

$$\frac{f}{P} = \frac{P}{P^*} \quad (13)$$

The simple relation given by Equation 13 will be found useful when no other data are available although it is decidedly inaccurate in the neighborhood of the critical state.

The fact that the  $\mu$ -chart, and the fugacity charts derived therefrom, are approximations must not be forgotten. They are valuable where more reliable data are lacking.

**Fugacity of Liquids and Solids.** Under most conditions the compressibilities of liquids and solids are small and at least as an approximation for any chosen material

$$\int V dP = V\Delta P, \text{ approximately}$$

$$\int V dP = NRT \ln \frac{f_2}{f_1} = V(P_2 - P_1), \text{ approximately} \quad (14)$$

For a solid or liquid in equilibrium with its vapor, the fugacity is the same as that of the vapor. When, as often happens, the pressure of the vapor is so low that the gas laws are applicable, the vapor pressure may be taken as equal to the fugacity.

<sup>1</sup> "Thermodynamics," p. 198, New York, McGraw-Hill, 1923.



**Activity.** Usually a ratio of fugacities is of greater utility than a single value. Often the determination of a single fugacity would be inconvenient or practically impossible. To overcome such difficulties, another function, the activity  $a$ , will be defined as

$$a = \frac{f}{f^0} \quad (15)$$

That is, the activity of a substance in any chosen state is the ratio of its fugacity in the state under discussion to its fugacity in some arbitrarily chosen standard state, both at the same temperature.

Relative to the standard state:

$$F - F^0 = \Delta F = NRT \ln a \quad (16)$$

**Choice of Standard States.** It is convenient to choose the reference states such that the laws of perfect solutions and perfect gases may be applied even to concentrated solutions and to gases at high pressure, without introducing error, simply by substituting, in these expressions, activities for the corresponding concentrations, mol fractions, or pressures. For this to be possible it is necessary that for each substance there be, at every temperature, a series of standard states, depending on the form in which it appears (as a component of a solution or a gas mixture).

For a gas or vapor it is generally assumed that

$$\frac{a}{P} = 1, \text{ when } P = 0$$

For either a liquid or solid acting as a *solvent*, the standard state is assumed to be the pure liquid or solid usually under an applied external pressure of 1 atm. If the gas laws may be applied to the vapor over the solution as well as the vapor over the pure *solvent*,

$$a_1 = \frac{P_1}{P_1^0} \quad (17)$$

where  $a_1$  is the activity of the solvent in solution,  $P_1$  its partial pressure over the solution, and  $P_1^0$  its pressure in a pure state at the same temperature. It is interesting to note that with the indicated reference state  $a_1/x_1 = 1$  when  $x = 1$ . Raoult's law is usually stated  $P_1 = P_1^0 x_1$ . It is easy to see that over all ranges for which this law holds  $a_1 x_1 = 1$ , while for concentrated, non-ideal solution  $a_1/x_1$  is a measure of the deviation of the solution from Raoult's law. On this basis a general form of Raoult's law applicable to concentrated solutions may be written

$$P_1 = P_1^0 x_1 \frac{a_1}{x_1} = P_1^0 a_1 \quad (18)$$

In this equation it is assumed that the vapor of the solvent follows the gas laws.

For a liquid acting as a *solute* the standard state is often so chosen that

$$\frac{a_2}{x_2} = 1, \text{ when } x_2 = 0$$

In dilute solutions Henry's law may be applied to the solute

$$P_2 = Kx_2$$

Over ranges when Henry's law is valid both of the preceding equations must hold. Therefore

$$\frac{\frac{f_2}{f_2^0}}{\frac{P_2}{K}} = 1$$

Moreover, at low concentrations it is desirable that  $P_2 = f_2$ . This can be so only if  $f_2^0$  is chosen equal to  $K$ .

**Activity Coefficients.** Often it will be desirable to use a function such that

$$\gamma c = a$$

where  $c$  is the concentration of the particular substance under discussion and  $\gamma$ , the activity coefficient, is a number such that the product  $\gamma c$  is equal to the activity. In general,  $\gamma$  is the quotient of activity divided by concentration.

Concentration may be expressed in several ways. For gases the mol fraction is often used. Under such conditions  $\gamma_x = \frac{a_x}{x}$ . The ratio  $\frac{a_1}{x_1}$  in

Equation 18 is an activity coefficient. Similarly, if concentration is expressed as weight-molality (mols solute per 1000 gm. of solvent),

$\gamma_m = \frac{a_m}{m}$ . For concentrations expressed as weight-molarity (mols of solute per 1000 gm. of solution),  $\gamma'_m = \frac{a'_m}{m}$ .

## SUMMARY

A reconsideration of the previous several pages indicates that the fugacity and activity functions were developed primarily to simplify calculation and interpretations. Both are intensive variables.

For any single substance the fugacity is a function such that as the material passes isothermally from state (1) to state (2)

$$\Delta F = NRT \ln \frac{f_2}{f_1}$$

Moreover, the numerical value of the fugacity is so fixed that for vapors in the gas-law range it is equal to the pressure.

The activity or relative fugacity is defined as

$$a = \frac{f}{f^0}$$

where  $f^0$  is the fugacity of the material in an arbitrarily chosen standard state. Relative to the standard state

$$F - F^0 = \Delta F = NRT \ln a$$

The activity coefficient is so defined that

$$\gamma = \frac{a}{c}$$

This is especially convenient when dealing with solutions where it has been the common practice to express composition in terms of concentration.

## NOTATION FOR CHAPTER XV

### *Upper Case:*

- $C$  Constant
- $F$  Free energy
- $K$  Henry's law constant
- $N$  Number of mols
- $P$  Absolute pressure
- $R$  Gas constant
- $T$  Absolute temperature
- $V$  Volume

### *Lower Case:*

- $a$  Activity
- $c$  Concentration
- $d$  Differential quantity
- $e$  Base of natural logarithms, 2.71828
- $f$  Fugacity
- $m$  Molality concentration, mols solute per 1000 gm. solvent
- $r$  Residual volume
- $x$  Mol fraction
- $z$  An exponent

*Subscripts:*

- $R$  Reduced quantity (ratio of value to value at critical state)  
 $m$  Molality concentration  
 $M$  Molal

*Superscripts:*

- <sup>0</sup> Standard state  
\* Refers to perfect-gas region

*Greek Letters:*

- $\Delta$  Value in final state — Value in initial state  
 $\mu$  Gas compressibility factor,  $PV/NRT$   
 $\gamma$  Activity coefficient

## PROBLEMS

1. Referring to Problem 6, Chapter X, calculate at 100°C. the activity of the solvent (water) at various concentrations. Make a plot of activity versus molal concentration.
2. Referring to Problem 7, Chapter X, on ammonia, calculate the fugacity and activity of both the ammonia and water at various concentrations (0 to 20 per cent  $\text{NH}_3$ ). Plot  $\log a$  versus  $c$  ( $a$  = activity;  $c$  = molal concentration, mols solute per kilogram solvent).
3. With the aid of the steam tables, construct a fugacity chart ( $f/P$  versus  $P_R$ ) for water at a reduced temperature of 1.20.
4. Methane at 25°C. and 1 atm. is to be compressed reversibly and isothermally in a cylinder (not a compressor) to a final pressure of 100 atm. Estimate, using the fugacity chart, the necessary work per mol of gas handled.
5. Gaseous pentane is compressed isothermally at 160°F. from 1 atm. to 500 lb./sq. in. abs. and expelled. With the use of the fugacity chart, estimate the work in B.t.u. required per pound mol of gas.

## CHAPTER XVI

### EQUILIBRIUM CONSTANTS

In Chapter III the general concept of a state or condition of equilibrium was discussed at some length, but from a distinctly qualitative aspect. Here these ideas will be amplified and considered quantitatively. The simple single phase (homogeneous) gas systems will first be studied, then those of a more complex, multiphase, heterogeneous nature. For simplicity, isothermal changes only are considered at this time. The effects of varying temperatures will be discussed later.

**General Considerations.** The equation



represents a chemical reaction in which  $a$  molecules of substance  $A$  and  $b$  molecules of substance  $B$  react to yield  $c$  molecules of  $C$  and  $d$  molecules of  $D$ . The accepted custom is to write the equation for any chosen reaction so that the reactants are on the left side and the resultants are on the right.

If a quantity of either  $A$  and  $B$ ,  $C$  and  $D$ , or a mixture of all four, is allowed to react chemically, at equilibrium, *all four* materials are always present.<sup>1</sup> This may be experimentally verified for a great many reactions, and constantly improved methods for detecting small quantities lead to the belief that it is true for all.

As is so often the practice in thermodynamics, it will be convenient to choose, in place of the actual path followed by the reacting substances, an equivalent series of paths more readily visualized. Consider any reaction, *e.g.*, that given by Equation 1, as proceeding in the following manner. First the reactants are changed reversibly and isothermally from their original state to the condition they will attain at equilibrium, yielding during the change a certain amount of energy as work. Next the resultants will be changed reversibly and isothermally from their states at equilibrium to the final condition they will have as resultants. None of these changes involves chemical reaction; all are but physical processes. A third step is necessary: to react chemically,  $A$  and  $B$

<sup>1</sup> Products of any other possible chemical reactions between the four primary substances will also be present, but for simplicity assume that  $A$ ,  $B$ ,  $C$ , and  $D$  represent the *only* possible materials.

forming  $C$  and  $D$ . This takes place isothermally at equilibrium and therefore neither requires nor yields any net work. The sum of the net isothermal work effects for these three steps must be the same as would have resulted had any other reversible isothermal path been chosen between the initial and final states.

**Equilibrium Constants — Perfect Gases.** Reactions involving only perfect gases will be considered first. Let the reaction be given by Equation 1. All changes will be reversible and isothermal. The symbols  $A_1$  and  $B_1$  will refer to  $A$  and  $B$  in their original states;  $C_2$  and  $D_2$  will refer to  $C$  and  $D$  in their final states. In this discussion the initial pressures for  $A$  and  $B$  and the final pressures for  $C$  and  $D$  are arbitrarily chosen. At equilibrium conditions the symbols  $A_e$ ,  $B_e$ ,  $C_e$ , and  $D_e$  will be used for the various materials. As previously suggested, instead of proceeding directly the reaction will be carried out by a series of reversible isothermal processes and the net result obtained by a summation of the individual steps. For equipment, four reversible, isothermally acting gas compressors will be required and in addition a constant-volume reaction chamber<sup>1</sup> assumed fitted with four semi-permeable membranes. Each membrane is permeable to one of the four reaction materials. This chamber is also so constructed that it may be kept at constant temperature (Figure 1). So operate the compressors that the following processes are carried out simultaneously:

<i>Process</i>	<i>Net Reversible Isothermal Work Effect</i>
1. Take into the first compressor $a$ mols of $A$ at the original partial pressure of $A$ , $P_{A1}$ . Expand this to the partial pressure $A$ will have at equilibrium, and discharge $A$ from the compressor and into the box at $P_{Ae}$ .	$aRT \ln \frac{P_{Ae}}{P_{A1}}$
2. Repeat process 1 for $B$ using compressor 2.	$bRT \ln \frac{P_{Be}}{P_{B1}}$
3. Take into the third compressor $c$ mols of $C$ from the box at the equilibrium partial pressure of $C$ , $P_{Ce}$ ; compress this to its final pressure $P_{C2}$ .	$cRT \ln \frac{P_{C2}}{P_{Ce}}$
4. Repeat process 3 for $D$ using compressor 4.	$dRT \ln \frac{P_{D2}}{P_{De}}$

The box is assumed to contain at all times at least a differential quantity of the reaction mixture under equilibrium conditions. As the reactants, at pressures corresponding to their equilibrium partial

<sup>1</sup> The reaction chamber is usually called a van't Hoff equilibrium box.

pressures, are added to the box held at constant volume and the results simultaneously withdrawn, the chemical reaction proceeds reversibly. The necessary quantity of heat is allowed to pass to or from the reaction chamber to hold the temperature constant.

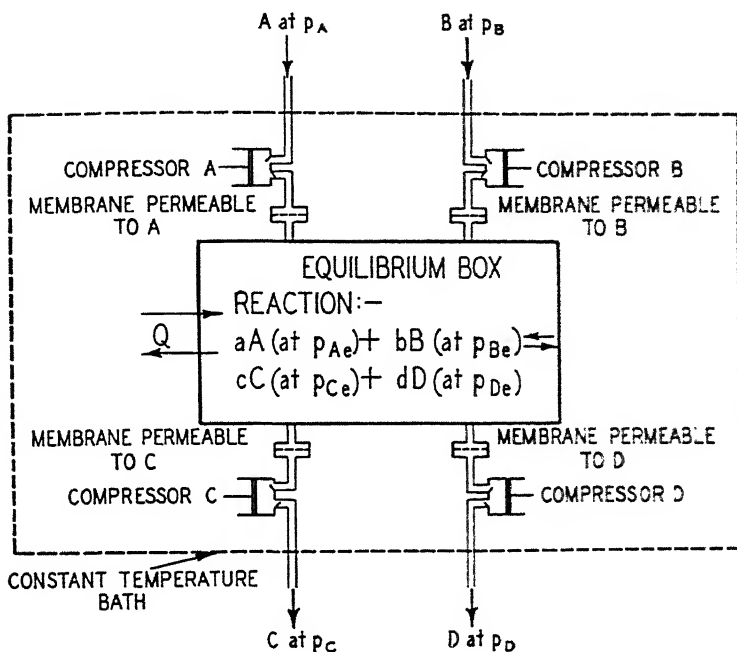


FIG. 1. Equilibrium Box.

The entire change has been so carried out that all work effects are of the familiar reversible isothermal compression or expansion types. The net work for the whole process must be the sum of these.

$$\begin{aligned}
 -W_{\text{net}} &= RT \left[ a \ln \frac{P_{Ae}}{P_{A1}} + b \ln \frac{P_{Be}}{P_{B1}} \right. \\
 &\quad \left. + c \ln \frac{P_{C2}}{P_{Ce}} + d \ln \frac{P_{D2}}{P_{De}} \right] \\
 &= RT \ln \frac{P_{Ae}^a P_{Be}^b}{P_{Ce}^c P_{De}^d} - RT \ln \frac{P_{A1}^a P_{B1}^b}{P_{C2}^c P_{D2}^d} \\
 W_{\text{net}} &= RT \ln \frac{P_{C2}^c P_{D2}^d}{P_{Ae}^a P_{Be}^b} - RT \ln \frac{P_{C2}^c P_{D2}^d}{P_{A1}^a P_{B1}^b} \quad (2)
 \end{aligned}$$

In the first term of the above equation the group made up of the four pressures is called the equilibrium constant for the reaction and when expressed in terms of pressure is usually designated by  $K_p$ . The second group of pressures has a similar form and may well be given the symbol  $K'_p$ . Equation 2 may now be written

$$W_{\text{net}} = RT \ln K_p - RT \ln K'_p \quad (3)$$

$$-\Delta F = RT \ln K_p - RT \ln K'_p \quad (4)$$

Experimentally it is found that, for a reaction in which all materials involved are perfect gases,  $K_p$  is at any chosen temperature a constant and not a function of the relative amounts of the various materials present at equilibrium.

That this must be true may readily be seen if one remembers that the net isothermal reversible work, as calculated from Equation 2, is a point function, *i.e.*, dependent only on initial and final conditions. These determine the value of the second term on the right-hand side of Equation 2. For fixed initial and final conditions, the first term on the right side of Equation 2 must have a fixed value, irrespective of the total pressure on the system at equilibrium — otherwise the isothermal reversible work,  $W$ , could not have been constant. One must not conclude from this, however, that the relative quantities of the various constituents present at equilibrium are independent of pressure at constant temperature.

**Equilibrium Constants and Standard Free Energy.** Referring to Equation 2 it is evident that if at the beginning as well as at the end all components are at unit pressure (each component is at unit partial pressure — this does not mean that the mixture pressure is unity), then the second term becomes  $RT \ln 1$ . Since  $\ln 1$  is zero, Equation 2 reduces to

$$\Delta F^0 = -RT \ln K_p \quad (5)$$

This is called a standard free energy change, and in general it is *only* under such "standard" conditions that the free energy change is equal to  $-RT \ln K_p$ . In addition it is customary to indicate the temperature level of the reaction; thus for a reaction carried out at 25°C. or 298°K.

$$\Delta F_{298}^0 = -RT \ln K_p$$

**Equilibrium Constants — General Case.** In 1864 Guldberg and Waage proposed the law of mass action. They stated that for any chemical reaction at any chosen temperature one might always write an expression of the form (referring to Equation 1)

$$\frac{[C]^c [D]^d}{[A]^a [B]^b} = \text{a constant} \quad (6)$$



The terms  $[A]$ ,  $[B]$ ,  $[C]$ , and  $[D]$  were called the active masses of the various materials. For reactions involving perfect gases it was found possible to use partial pressures as active masses, while in dilute solutions of non-ionized substances concentrations could be used. However, the general problem of determining "active mass" remained unsolved until after a full understanding of the second law principle had been developed.

In the preceding chapter a function called the activity was so defined that the net reversible isothermal work effect produced when a substance passed from condition (1) to condition (2) would always be given, as far as that substance was concerned, by

$$-W_{\text{net}} = \Delta F = NRT \ln \frac{a_2}{a_1} \quad (7)$$

It must be evident that an equation similar to (2) could have been derived in terms of activities instead of partial pressures. Theoretically this involves no difficulty. Practically it would require, instead of the simple pump, some device capable of so adapting itself that it could always produce or absorb work with a corresponding change in activity irrespective of the kind of material handled.<sup>1</sup> The substitution of activities for partial pressures in Equation 2 immediately removes the limitation that the substances involved must be perfect gases. They can be any desired materials, and in general for any reaction carried out isothermally and reversibly

$$W_{\text{net}} = RT \ln \frac{a_c^c a_d^d}{a_a^a a_b^b} - RT \ln \frac{a_c^c a_d^d}{a_a^a a_b^b} \quad 8$$

$$\Delta F = -RT \ln K_a + RT \ln K'_a \quad 9$$

$$\Delta F^0 = -RT \ln K_a \quad 10$$

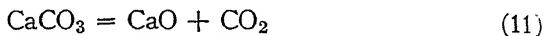
Some of the advantages of the activity function can now be appreciated. It is equivalent to the "active mass" of Guldberg and Waage. If the standard state is properly chosen, the activity reduces to the

<sup>1</sup> As a matter of fact, one might use the simple gas compressor previously mentioned for practically every case. Throughout this discussion some definite fixed temperature is assumed, and at every state each material will have a definite vapor pressure. At ordinary temperatures this pressure may be extremely small for solids, but it is nevertheless fixed. Instead of reacting directly on the liquid (or solid), it may first be converted to a vapor under equilibrium conditions, this vapor compressed, and finally the vapor condensed once more at a second equilibrium condition to yield the material in the desired final state. By such a series of processes any material may be visualized as transformed from one state to another. In such transformations the only step involving a net work effect is the vapor compression.

pressure when the gas laws apply and to the concentration when the laws of dilute solutions hold, thus leading to the same result as was obtained experimentally by early workers in this field. Use of the activity function makes the simple law of mass action valid in all cases. At one stage in the development of thermodynamics there was the choice between either abandoning the mass-action law or developing some corrective function similar to activity. The latter course having been chosen, the difficulties now arise in the calculation and correlation of activities — once tabulated their use is comparatively simple.

### HETEROGENEOUS EQUILIBRIUM CONSTANTS

For the reaction



knowing nothing of the state of the various substances one would in general write

$$K_a = \frac{a_{\text{CO}_2} a_{\text{CaO}}}{a_{\text{CaCO}_3}} \quad (12)$$

But up to moderate pressures the volumes of solids and liquids are small in comparison with those for gases. Moreover, for these the activity is practically a function of temperature only, although care must be exercised in making such an assumption for liquids as the critical condition is approached.

Without serious error it may be assumed in Equation 12

$$a_{\text{CaO}} = a_{\text{CaCO}_3} \cong 1$$

If this is done for reaction 11

$$K_a = a_{\text{CO}_2}$$

or as often written

$$K_p = P_{\text{CO}_2} \quad (13)$$

Expressed as in (12) this might be called the heterogeneous equilibrium constant for the reaction while (13) could be given as the expression for the homogeneous equilibrium constant.<sup>1</sup>

**Effect of Concentration.** In general, increasing the concentration of any constituent increases its activity but does not change, at a given temperature, the value of the equilibrium constant. To make a reaction proceed more completely (obtain larger yields) it is necessary either to

<sup>1</sup> Usage does not seem standardized, and some authors interchange the designations here suggested.

increase the activities of the reactants or decrease those of the resultants.

This method is indicated by the mass-action expression and is familiar to all workers in chemistry. Often it is economically expedient to adopt some method of keeping the activities of the resultants low rather than to increase the activities of the reactants. The chemical engineer accomplishes this by a recycling process in which a certain small yield is obtained at each pass, the product removed, and the unreacted materials returned for recycle, as in the manufacture of synthetic ammonia. Sometimes a reagent capable of reacting with one of the products is added, in this way the activity (concentration) of that product being kept low. Often this may be a selective absorbent for the material in question. More common in previous years than now was the practice of using an excess of reactants. Operators of the Solvay process are accustomed to use an excess of the inexpensive reactant sodium chloride to obtain high yields. In addition the foregoing methods also have the advantage of giving increased rate—a question beyond the scope of thermodynamics.

**Phase Equilibrium.** For any system, irrespective of its complexity, there is at equilibrium a necessary relation between the number of constituents (components), the phases, and the variance (true intensive variables) as given by the phase rule of Gibbs

$$V = C + 2 - P \quad (14)$$

That this must be true is readily proved by a consideration of the basic second law principle. In a system at constant temperature and pressure throughout, the ability of any constituent to do work is a function solely of its activity. A given component at the same activity in two phases can yield no net work in going from one phase to the other—there is no tendency or urge for it to move—it is at equilibrium.<sup>1</sup>

To fix the state of a component in any phase one must specify only its pressure, temperature, and activity.

Consider any single-phase system of  $C$  components. To fix all truly intensive properties of such a system, specify the pressure, the temperature, and  $C - 1$  concentrations. Since in any single phase at fixed pressure and temperature the activity of a component is some function of its concentration, one need specify only  $C - 1$  concentrations to fix all—it is not necessary to fix  $C$  concentrations. For a single phase,  $C - 1 + 2 = C + 1$  intensive variables must be fixed.

<sup>1</sup> This assumes that the activity of the component in question is determined relative to the same standard or reference state in the two phases and not to different standards as is sometimes done.

If equilibrium is to prevail in a multiphase system of  $P$  phases the pressure and temperature must be the same in all phases. To determine such a system  $P(C - 1)$  concentrations and, in addition, the pressure and temperature must be fixed. Since for equilibrium the activity of each component must be the same in all phases,  $(P - 1)$  independent relations equating the activity of each component in the various phases may be written, a total of  $C(P - 1)$  equations. The total number of independent variables to be specified is then

$$V = P(C - 1) + 2 - C(P - 1)$$

$$V = C + 2 - P$$

### SUMMARY

The major ideas presented in this section are:

1. The derivation in terms of isothermal reversible work quantities of the "mass-action" expression for reactions involving only perfect gases.
2. The development, by the general concept of activity, of a generalized "mass-action" expression applicable to any reaction.
3. The limitations to be kept in mind when using the equation

$$-\Delta F^0 = RT \ln K_a$$

namely, unit activity for reactants and resultants.

4. The derivation of a generalized interphase relationship for equilibrium conditions

$$V = C + 2 - P$$

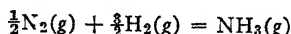
the phase rule of Willard Gibbs.

### PROBLEMS

1. Dodge and Larson give the following values for  $K_p$ , the equilibrium constant, for the formation of ammonia from the elements at 500°C. (*J. Am. Chem. Soc.*, 45, 2918 [1923]; 46, 367 [1924].)

$p$ , atm.	10	300	600
$K_p(p = \text{atm.})$	0.00381	0.00498	0.00651

according to the reaction



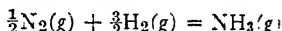
Clearly stating all assumptions, calculate at 500°C. the equilibrium constants,  $K_a$  in terms of activities,  $K_x$  in terms of mol fractions and  $K_c$  in terms of concentrations (mols per liter). Assume that the fugacity of a constituent of a gaseous mixture is the fugacity of the constituent in a pure state, as a gas at mixture temperature and pressure, multiplied by its mol fraction in the mixture. For  $P$ - $V$ - $T$  relations, use the  $\mu$ -chart.

2. It is proposed to manufacture hydrogen peroxide by reacting oxygen gas at high pressure with liquid water at 25°C. Do you recommend undertaking a research program to study this proposal?

Data:  $\text{H}_2 + \text{O}_2 = \text{H}_2\text{O}_2(\text{dilute}); \Delta F_{298}^0 = -31,470 \text{ cal. gm. mol}$

$\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O}(l); \Delta F_{298}^0 = -56,560 \text{ cal. gm. mol}$

3. What is the maximum conversion to ammonia obtainable in a Haber unit operating at 300 atm. pressure and 500°C., when stoichiometric quantities of gas are used? Neglect the presence of argon.



$$12.31T \log T - 12.30T + \frac{8.45}{10^7} T^3 - 9170 \text{ cal. mol NH}_3 \text{ } ^\circ\text{K}.$$

*Rev.*, 36, 750 [1930]).

4. For the reduction of iron oxide, algebraically set up the two equilibrium constants (one homogeneous, the other heterogeneous). Calculate the equilibrium constant  $K_a$  for the reaction



5. Show that increasing the total pressure results in higher yields of products at equilibrium for reactions proceeding with a decrease in volume and lower yields for those proceeding with an increase in volume.

6. Show that, even if the assumption is not made that all components appear in all phases of a multiphase system, the same expression results for the phase rule.

## CHAPTER XVII

### EFFECTS OF PRESSURE, VOLUME, AND TEMPERATURE ON THERMODYNAMIC PROPERTIES OF SUBSTANCES

At this point a somewhat detailed study will be made of effects resulting from variation in the three important variables, pressure, volume, and temperature. Except for a few simple cases these have so far not been studied quantitatively. This omission was intentional so that a firm grasp could be had of the more fundamental concepts of thermodynamics without the complicating effects that consideration of these variables might introduce. Discussion here will be much simplified and not unduly circumscribed by limiting it to the more important thermodynamic functions heretofore presented.

**General Considerations.** Without doubt the quickest and most concise way of arriving at the results attained in this chapter is to resort to methods often practiced by the expert mathematician, that of manipulating equations and finally arriving at the sought relation. Another method is to try to visualize each step and eventually obtain an answer, the path to which has been characterized by a series of mental pictures as to what has been occurring. To a certain extent both approaches will be employed in this chapter.

Here a review of a few mathematical relations may be desirable. Remember that most thermodynamic systems of interest to engineers are those of but two independent variables. In the language of mathematics this fact may be expressed by saying that  $z$  is some function of  $x$  and  $y$

$$z = \phi(x, y) \quad (1)$$

Differentiation yields

$$dz = \left( \frac{\partial z}{\partial x} \right)_y dx + \left( \frac{\partial z}{\partial y} \right)_x dy \quad (2)$$

Equation 2 merely states that the total differential change in  $z$  is equal to that due to changing  $x$  holding  $y$  constant, times the change in  $x$ , plus that due to changing  $y$  holding  $x$  constant, times the change in  $y$ . Reference may be made to any good textbook on differential calculus for the proof of this. It is often helpful to remember that the expression  $\left( \frac{\partial z}{\partial x} \right)_y$  is geometrically the slope of the

$z$ - $x$  curve at some constant value of  $y$  (Figure 1). To indicate geometrically the three variables  $x$ ,  $y$ , and  $z$  requires a surface. Figure 2 represents a plane passed through such a surface at a chosen value of  $y$  and parallel to both the  $z$  and  $x$  axes.

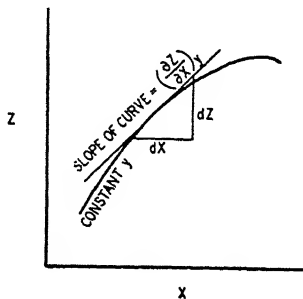


FIG. 1.

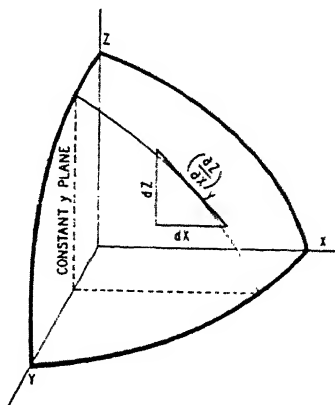


FIG. 2.

For changes such that  $dz = 0$

$$\left(\overline{\partial y}\right) = \frac{-\left(\frac{\partial z}{\partial y}\right)_x}{\left(\frac{\partial z}{\partial x}\right)_y} \quad (3)$$

Equation 2 may be written

$$dz = M dx + D dy$$

where  $M = \left(\frac{\partial z}{\partial x}\right)_y$  and  $D = \left(\frac{\partial z}{\partial y}\right)_x$ . But  $\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right) = \frac{\partial^2 z}{\partial x \partial y}$  and  $\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right) = \frac{\partial^2 z}{\partial x \partial y}$ , or using the symbols  $M$  and  $D$

$$\frac{\partial M}{\partial y} = \frac{\partial D}{\partial x} \quad (4)$$

Equation 5 is usually called Euler's criterion<sup>1</sup> for integrability.

A differential having the characteristics of  $dz$  is known as a complete or perfect differential. The differential of any point function is complete or perfect. Thus  $dH$ ,  $dE$ ,  $dS$ ,  $dF$ ,  $dA$ , are all of this type. On the other hand,  $dW$  and  $dQ$  in general are not perfect differentials.

<sup>1</sup> Mellor, "Higher Mathematics for Students of Chemistry and Physics," p. 70, London, Longmans, Green & Co.; or Woods "Advanced Calculus," pp. 73-74, Boston, Ginn & Co., 1934.

## MAXWELL RELATIONS

Many important thermodynamic relations are readily obtained directly from the appropriate point functions by using the relation

$$\frac{\partial M}{\partial y} = \frac{\partial D}{\partial x}$$

The more important partial differential expressions between the different variables, of which a great many are possible, are known after their proposer as the Maxwell relations. A few are given in Table I.

TABLE I  
MAXWELL RELATIONS

Function	Differential	Maxwell Relation
$\Delta E = Q - W$	$dE = T dS - P dV$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$
$H = E + PV$	$dH = T dS + V dP$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$
$A = E - TS$	$dA = -S dT - P dV$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
$F = H - TS$	$dF = -S dT + V dP$	$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

The utility of these relations may be illustrated by applying the third relation in Table I to a monovariant change.

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

In this connection it may be helpful to have a definite system in mind, *e.g.*, a cylinder filled partly with liquid and partly with vapor in equilibrium with the liquid. But since the change is monovariant there is but one independent variable anyway and

$$\frac{dP}{dV} = \frac{dS}{\Delta V} = \frac{\Delta S}{T \Delta V} = \frac{\Delta H}{T \Delta V} \quad (5)$$

This is the familiar Clapeyron equation,  $Q_P$  being the heat effect due to the change.

By holding certain of the variables constant another set of relations is obtained, Table II.



TABLE II  
RELATIONS FOR THERMODYNAMIC PROPERTIES

Differential	Independent Variable Held Constant	Relation
$dE = T dS - P dV$	$S$	$\left(\frac{\partial E}{\partial V}\right)_S = -P$
	$V$	$\left(\frac{\partial E}{\partial S}\right)_V = T$
$dH = T dS + V dP$	$S$	$\left(\frac{\partial H}{\partial P}\right)_S = V$
	$P$	$\left(\frac{\partial H}{\partial S}\right)_P = T$
$dA = -S dT - P dV$	$T$	$\left(\frac{\partial A}{\partial V}\right)_T = -P$
	$V$	$\left(\frac{\partial A}{\partial T}\right)_V = -S$
$dF = -S dT + V dP$	$T$	$\left(\frac{\partial F}{\partial P}\right)_T = V$
	$P$	$\left(\frac{\partial F}{\partial T}\right)_P = -S$

By equating those various terms in the third column which are equal one may obtain

$$\left(\frac{\partial E}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P$$

$$\left(\frac{\partial E}{\partial V}\right)_S = \left(\frac{\partial A}{\partial V}\right)_T$$

$$\left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial F}{\partial P}\right)_T$$

$$\left(\frac{\partial F}{\partial T}\right)_P = \left(\frac{\partial A}{\partial T}\right)_V$$

Several thousand expressions connecting the eight important functions  $P$ ,  $V$ ,  $T$ ,  $S$ ,  $E$ ,  $H$ ,  $F$ , and  $A$  may be derived, but most of them are of but little importance in engineering work.<sup>1</sup>

<sup>1</sup> See Bridgman, *Phys. Rev.*, 2, 3, 273 (1914) for a simplified method of tabulating these, or Sherwood and Reed, "Applied Mathematics in Chemical Engineering," New York, McGraw-Hill, 1939, p. 178.

Although changes in the various point functions do not depend on the path, nevertheless to use most of the relations in the above tables a reversible path must be chosen for the process under discussion.

**Enthalpy.** The familiar heat capacity at constant pressure is  $\left(\frac{\partial H_M}{\partial T}\right)_P$ .

In a Joule-Thomson expansion the coefficient  $\mu$  is defined by the equation

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H \quad (6)$$

But along a constant enthalpy<sup>1</sup> path  $dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = 0$ .

Therefore

$$\begin{aligned} \left(\frac{\partial T}{\partial P}\right)_H &= \frac{-\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P} \\ -\left(\frac{\partial H_M}{\partial P}\right)_T &= \mu C_p \end{aligned} \quad (7)$$

Equation 7 shows the rate at which heat must be absorbed per unit change in pressure during a flow process carried out irreversibly and isothermally and with no appreciable kinetic or potential energy effects.

Since

$$H = E + PV,$$

$$dH = dE + P dV + V dP$$

But  $dE = T dS - P dV$  for reversible cases; therefore

$$dH = T dS + V dP \quad (8)$$

or

$$V = -T \left(\frac{\partial S}{\partial P}\right)_T + \left(\frac{\partial H}{\partial P}\right)_T \quad (9)$$

But, as indicated in Table I,

$$-\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial S}{\partial P}\right)_T \quad (10)$$

Substituting in Equation 9,

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P \quad (11)$$

<sup>1</sup> The systems considered here are those of but two independent variables. Magnetic, gravitational, surface, and similar effects are neglected.

Equation 11 is interesting for several reasons. It is often called a general *thermodynamic equation of state*. For any system it gives a necessary relation between  $P$ ,  $V$ ,  $T$ , and enthalpy. Moreover, it shows how the enthalpy of a system must change with pressure along an isothermal path, namely, that at any chosen point the slope of the  $H$ - $P$  curve at constant temperature must equal the volume minus the product of the slope at constant pressure for the  $V$ - $T$  curve and the temperature. Usually, to get  $(\Delta H)_T$  between two desired values of pressure, resort must be made to graphical integration plotting  $V-T\left(\frac{\partial V}{\partial T}\right)_P$  versus  $P$  along the required isothermal. The area under the curve

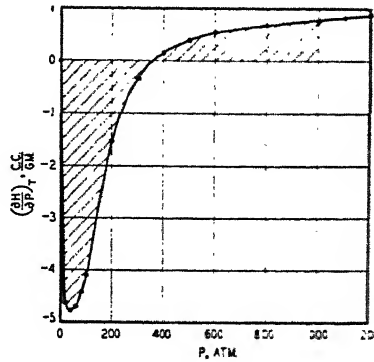


FIG. 3. Graphical representation to Evaluate Enthalpy Change with Pressure. Values are for Nitrogen at  $-70^\circ\text{C}$ . Deming and Shupe, Phys. Rev., 37, 643; 1931.

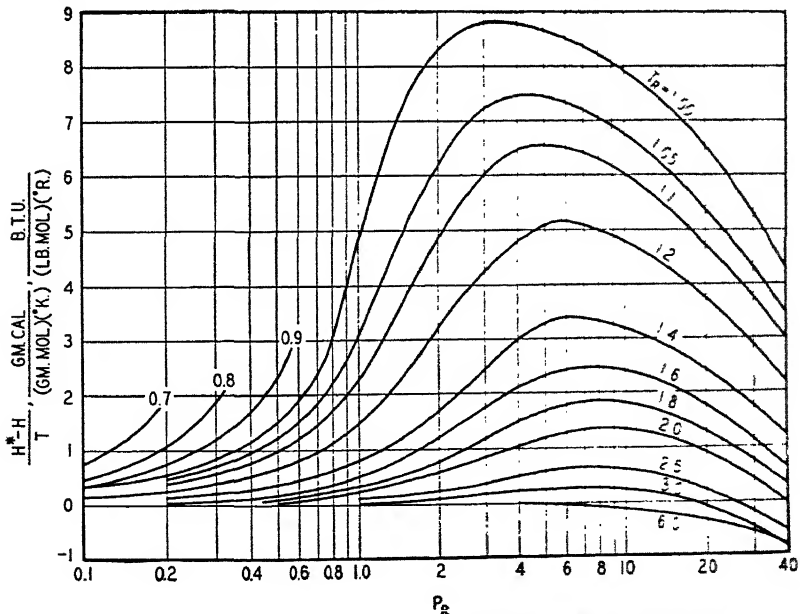


FIG. 4. Change of Enthalpy with Pressure at Constant Temperature.

between any two desired values of  $P$  is  $(\Delta H)_T$ . Figure 3 shows this graphically for nitrogen.

Equation 11 clearly indicates that if there is a group of substances whose  $P$ - $V$ - $T$  relations on a reduced basis are common, as is true of materials following the  $\mu$ -charts, then for all these a common plot for the effect of pressure on enthalpy is possible. Figure 4<sup>1</sup> is such a plot.<sup>2</sup>

For any material, Equation 11 clearly shows the change in enthalpy at constant temperature to be independent of thermal values (heat capacities) and dependent only on  $P$ - $V$ - $T$  relations.

A general method for getting the approximate change in enthalpy of gases or vapors where data are limited may now be outlined. Assume that the enthalpy change is desired between two points  $A$  and  $B$  not at the same temperature and each at a pressure such that the gas laws may

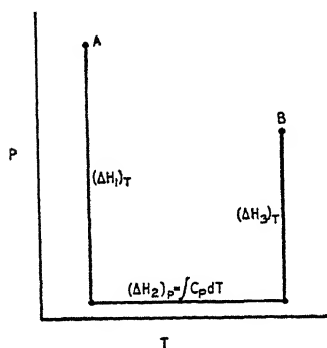


FIG. 5. Three-Step Method for Evaluating Changes in Enthalpy.

not be applied. Referring to Figure 5, by a three-step path pass from  $A$  isothermally to a pressure where the gas laws are applicable and calculate  $(\Delta H_1)_T$  by the aid of Figure 4. Pass at constant pressure, in the gas-law region, from  $T_A$  to  $T_B$ , getting  $(\Delta H_2)_P$  by the relation

$$C_p dT. \text{ Proceed isothermally at } T_B \text{ from the low-pressure gas-law region to the final observed pressure } P_B \text{ getting } (\Delta H_3)_T \text{ by Figure 4. The total enthalpy change is}$$

$$\Delta H = (\Delta H_1)_T + (\Delta H_2)_P +$$

**Internal Energy.** From Table I it is seen that  $dE = T dS - P dV$ . By a procedure analogous to that used in the previous section a second thermodynamic equation of state

$$\left( \frac{\partial E}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P \quad (12)$$

may be derived. This makes possible calculation of change in internal energy with volume at constant temperature. The more useful change with pressure at constant temperature is perhaps most readily obtained from values of  $(\Delta H)_T$  by the simple expression

$$(\Delta H)_T = (\Delta E)_T + \Delta(PV)_T$$

<sup>1</sup> Brown, Lewis, and Weber, *Ind. Eng. Chem.*, 26, 325 (1934); Watson and Smith, *National Petroleum News*, July 1, 1936.

<sup>2</sup> Often it is convenient to use the relation  $\left( \frac{d \ln f}{dT} \right)_P = \frac{H^* - H}{NRT^2}$  for the actual construction of these plots.

The three-step path outlined in the previous section is often a convenient method for getting change in internal energy where the  $\mu$ -charts or plots derived from them are involved. In general, determination of internal energy changes is of less importance to engineers than changes in enthalpy.

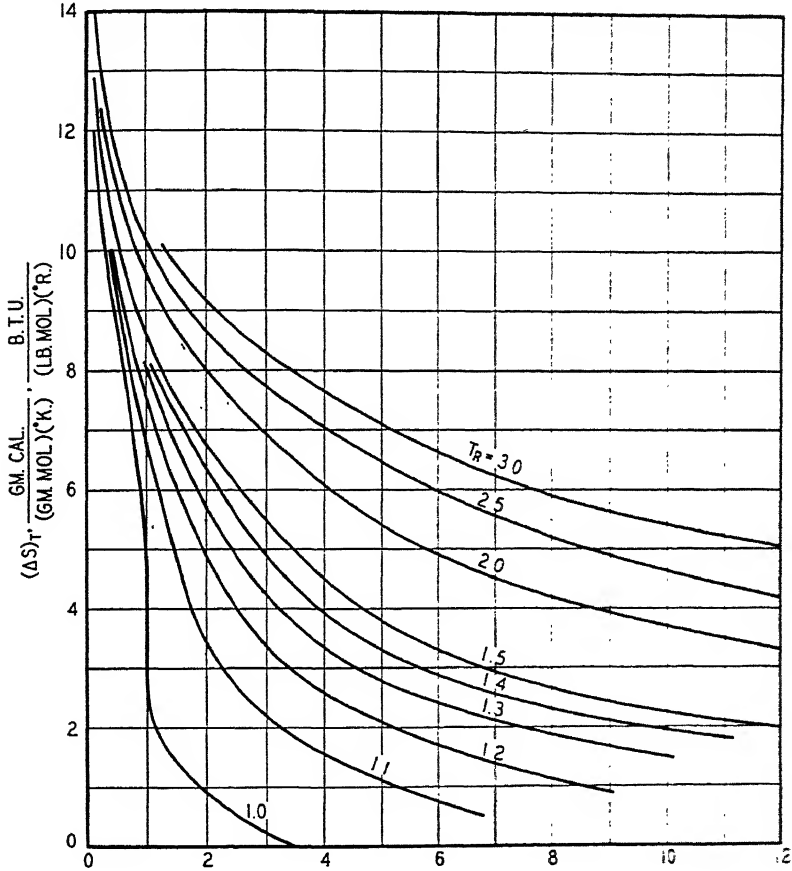


FIG. 6. Change of Entropy with Pressure at Constant Temperature

**Entropy.** Along a constant-volume path

$$\left( \frac{\partial T}{\partial V} \right)_V = T$$

while along a constant-pressure path

$$\left( \frac{\partial S_M}{\partial T} \right)_P = \frac{C_p}{T}$$

Expressions for change in entropy with pressure (or volume) at constant temperature have already been derived:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad (10)$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad (13)$$

Using Equation 10 expressed in terms of reduced functions, Figure 6 has been constructed for materials following the  $\mu$ -charts.

**Free Energy.** This point function is defined by the equation

$$F = H - TS$$

Differentiating with respect to  $T$  at constant  $P$

$$\left(\frac{\partial F}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P - T\left(\frac{\partial S}{\partial T}\right)_P - S \quad (14)$$

But along a constant-pressure path

$$dH = T dS$$

Therefore

$$\left(\frac{\partial F}{\partial T}\right)_P = -S = \frac{F - H}{T} \quad (15)$$

In Table II this same equation was obtained from the last relationship.

If Equation 15 is applied to the reactants and to the resultants of a chemical reaction carried out at two temperature levels, both under the same restraints of pressure,

$$\left(\frac{\partial(\Delta F)}{\partial T}\right)_P = -\Delta S = \frac{\Delta F - \Delta H}{T} \quad (16)$$

Rearranging

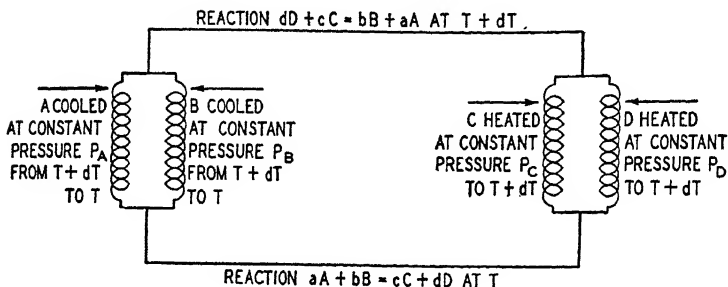
$$\Delta F = \Delta H + T\left(\frac{\partial \Delta F}{\partial T}\right)_P \quad (17)$$

In this form (17) is usually called the Gibbs-Helmholtz equation.

Under these conditions the subscript  $P$  does not necessarily mean that the pressures on all reactants and resultants must be the same at the different temperature levels but only that at one temperature level the pressure on a given substance must be the same as it was at the other temperature, although the pressures on the various materials involved may be different.

The important relation for change in free energy with temperature may be visualized with the aid of Figure 7.

Consider a general reaction such as  $aA + bB = cC + dD$ . Let this be carried out reversibly and isothermally at constant *total* pressure yielding a net work effect  $\Delta F$  and absorbing a heat  $Q$  at  $T$ . As indicated, next pass the resultants through separate heaters (separate to prevent chemical reaction) where each is heated at constant pressure to  $T + dT$ . This requires for each a heat absorption



NOTE THAT THE PRESSURES  $P_A, P_B, P_C$  AND  $P_D$   
ARE NOT NECESSARILY EQUAL

FIG. 7. Diagram to Illustrate Change in  $\Delta F$  with Temperature.

$NC_p dT$ . Now allow the reaction to proceed in reverse direction at  $T + dT$  reversibly and isothermally at constant *total* pressure absorbing a net work  $\Delta F + d(\Delta F)$  and absorbing an amount of heat  $Q + dQ$ . Now pass the reactants through separate constant-pressure coolers until the original state at  $T$  is attained. The heat rejected in the last step would be for each reactant  $NC_p' dT$ .

Relative to  $Q$ , the heat effects during the constant-pressure heatings and coolings are negligible. But at  $T + dT$ , a heat effect of  $Q + dQ$  has an ability to do work equal to  $Q dT/T$  relative to a temperature level  $T$ .

The preceding steps constitute a reversible cyclical process for which

$$\Delta F - (\Delta F + d\Delta F) - \frac{Q dT}{T} = 0$$

$$\left( \frac{\partial(\Delta F)}{\partial T} \right)_P = - \frac{Q_{\text{rev}}}{T} = -\Delta S \quad (16)$$

#### CALCULATION OF FREE ENERGY AS A FUNCTION OF TEMPERATURE

Since 
$$d\left(\frac{\Delta F}{T}\right) = \left(\frac{1}{T}\right) d\Delta F - \left(\frac{\Delta F}{T^2}\right) dT$$

(elementary calculus) and since

$$d(\Delta F) = \left( \frac{\Delta F - \Delta H}{T} \right) dT$$

it follows that

$$\begin{aligned} \left( \frac{\Delta F}{T} \right) &= \left( \frac{\Delta F}{T^2} \right) \Delta H \\ \frac{d \left( \frac{\Delta F}{T} \right)}{dT} &= \frac{\Delta H}{T^2} \end{aligned} \quad (18)$$

$$\frac{d\left(\frac{\Delta F}{T}\right)}{d\left(\frac{1}{T}\right)} = \Delta H \quad (19)$$

If  $\Delta H$  is known as a function of  $T$ , either (18) or (19) may be integrated to give an equation expressing  $\Delta F$  as a function of  $T$ . It will be remembered that  $\Delta H$ , the heat of reaction at constant pressure, may be expressed in terms of temperature by equations of the form

$$\Delta H = \Delta H_0 + \int \Delta C_p dT \quad (20)$$

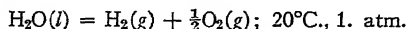
where  $\Delta C_p$  is the difference between the heat capacities of the resultants and the heat capacities of the reactants. The heat capacities are often given in terms of simple algebraic equations involving temperature as the only variable:

$$\Delta C_p = \alpha + \beta T + \gamma T^2 + \dots \quad (21)$$

This may be substituted in (20) and the resulting value of  $\Delta H$  substituted in (19). Integration then gives

$$\Delta F = \Delta H_0 - \alpha T \ln T - \frac{1}{2}\beta T^2 - \frac{1}{6}\gamma T^3 + \cdots IT \quad (22)$$

Equation 22 as derived is limited to cases where there is no change in phase of any of the materials on passing from one temperature level to another. For example, this equation as given is not applicable to the reaction



if the free energy change desired is for



Here the water has undergone a phase change (vaporization) in passing from one temperature level to the other. A second point of importance is that the constant of integration  $I$  has mathematical but no physical significance. Equations based on (22) are valid only between the temperature limits for which they are derived and must not be extended over other ranges.



By Equation 22, the free energy at any temperature level may be calculated provided that one has the heat of reaction,  $\Delta H_0$ , at some temperature; sufficient thermal data to determine the coefficients  $\alpha$ ,  $\beta$ ,  $\gamma$ ; and a single value of the free energy change. Thermal values are readily measured, but getting equilibrium data or their equivalent is usually less convenient. A way of circumventing this difficulty will be discussed in connection with the third law.

The effect of pressure on the free energy is readily obtained from

$$\Delta F = \int dF = \int V dP \quad (23)$$

This equation has been used several times in previous discussions. Differentiation with respect to  $P$  yields

$$\left( \frac{\partial F}{\partial P} \right)_T = V \quad (24)$$

**Fugacity.** The fugacity was so defined that for a given substance between any two isothermal states

$$\Delta F = F_2 - F_1 = NRT \ln \frac{f_2}{f_1} \quad (25)$$

Differentiating with respect to temperature, the pressure remaining constant<sup>1</sup>

$$\left( \frac{\partial F}{\partial T} \right)_P - \left( \frac{\partial F}{\partial T} \right)_P = \frac{\partial}{\partial T} \quad (26)$$

Now assume that the change indicated in (25) is an isothermal expansion of a vapor to a final state such that the gas laws may be applied. At constant pressure the fugacity of a material following the gas laws is equal to the pressure and certainly cannot change if the pressure is held constant. Then (26) reduces to

$$\left( \frac{\partial F_2}{\partial T} \right)_P - \left( \frac{\partial F_1}{\partial T} \right)_P = NR \ln \frac{f_2}{f_1} - NRT \left( \frac{\partial \ln f_1}{\partial T} \right)_P \quad (27)$$

Since

$$\left( \frac{\partial F}{\partial T} \right)_P = F - H$$

<sup>1</sup> The derivation here given follows that of Lewis, "Thermodynamics," New York, McGraw-Hill Book Co., 1923, pp. 200-201.

Equation 27 becomes

$$\left(\frac{\partial \ln f_1}{\partial P}\right)_T = \frac{H^* - H_1}{NRT^2}$$

But it must be remembered that (28) is true only if the final state is in the gas-law range. This equation is frequently employed to calculate the change in enthalpy with pressure at constant temperature from  $P$ - $V$ - $T$  data.

Change of fugacity with pressure is seen to be

$$\left(\frac{\partial \ln f}{\partial P}\right)_T = \frac{V_M}{RT}$$

**Activity.** Since activity is defined as relative fugacity, equations for the effect of pressure and temperature, analogous in form to those for fugacity, may be derived.

**Helmholtz Free Energy.** Equations for the effect of pressure and temperature on the Helmholtz free energy,  $A$ , are given in Table II.

**Equilibrium Constants.** Since  $\Delta F^0 = -RT \ln K_a$  the effect of temperature on  $K_a$  is readily obtained from Equations 18 and 19.

$$\begin{aligned} \frac{d \ln K_a}{dT} &= \frac{\Delta H}{RT^2} \\ \frac{d \ln K_a}{d \frac{1}{T}} &= -\frac{\Delta H}{R} \end{aligned} \quad (30)$$

A little thought will indicate that

$$\left(\frac{\partial \ln K_a}{\partial P}\right)_T = 0 \quad (31)$$

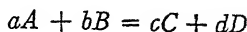
In deriving, by means of an equilibrium chamber, the expression

the sole limitation as to pressures in the chamber was that the various constituents were at whatever pressures were necessary for equilibrium — irrespective of the total pressure in the chamber. The limitation that each reactant and resultant must appear at unit activity was an assumption quite independent of conditions inside the chamber.

**Equilibrium Constants in Perfect Gas Systems.** In these one may substitute partial pressures for activities. They in turn are related to the total pressure by Dalton's law:

$$p_i = \pi y_i$$

Considering the reaction



if concentration is expressed in the usual units of mols per liter, i.e.,  $N/l$ , simple relations between the various equilibrium constants may be found

$$\begin{aligned} K_a &= K_p \\ K_c &= K_p (RT)^{(a+b)-(c+d)} \\ K_x &= K_p \pi^{(a+b)-(c+d)} \end{aligned} \quad (32)$$

In the gas-law range  $K_p$  and  $K_c$  are not functions of pressure, but  $K_x$  is.

To determine the effect of temperature let  $\Delta N = (c + d) - (a + b)$ . Then

$$\begin{aligned} \ln K_p &= \ln K_c + \Delta N \ln RT \\ \ln K_p &= \ln K_x + \Delta N \ln \pi \end{aligned} \quad (33)$$

But since

$$\begin{aligned} \ln K_a &= \ln K_p \\ \frac{d \ln K_p}{dT} &= \frac{\Delta H}{RT^2} = -\frac{Q_p}{RT^2} \end{aligned}$$

Therefore

$$\frac{d \ln K_c}{dT} = \frac{\Delta H}{RT^2} - \frac{\Delta N}{T} \quad (34)$$

$$\frac{d \ln K_x}{dT} = \frac{\Delta H}{RT^2} \quad (35)$$

Equilibrium constants for systems containing substances not perfect gases are best expressed in terms of activities only. Although, for constants in terms of concentrations, molalities, or mol fractions, simplification is sometimes possible by assuming the laws of perfect solutions or similar approximations, in general it is more convenient to limit discussions to  $K_a$ .

#### SUMMARY

The utility of the Maxwell relations as an aid in deriving thermodynamic relations was indicated.

The effects of temperature and pressure on the more important thermo-

dynamic functions were discussed, the particularly important equations

$$\left(\frac{\partial(\Delta F)}{\partial T}\right)_P = \frac{\Delta F - \Delta H}{T}$$

$$\frac{d \ln K_a}{dT} = \frac{\Delta H}{RT^2}$$

being developed.

Variation of the different equilibrium constants, for perfect gas systems, with temperature and pressure was studied.

## NOTATION FOR CHAPTER XVII

### *Upper Case:*

<i>A</i>	Helmholtz free energy
<i>B</i>	Availability function
<i>C</i>	Heat capacity
<i>E</i>	Internal energy
<i>F</i>	Free energy
<i>H</i>	Enthalpy
<i>I</i>	A constant
<i>K</i>	Equilibrium constant
<i>K<sub>a</sub></i>	Equilibrium constant in terms of activity
<i>K<sub>c</sub></i>	Equilibrium constant in terms of concentration
<i>K<sub>p</sub></i>	Equilibrium constant in terms of partial pressure
<i>K<sub>x</sub></i>	Equilibrium constant in terms of mol fraction
<i>N</i>	Number of mols
<i>P</i>	Absolute pressure
<i>Q</i>	Heat added to system
<i>R</i>	Gas constant
<i>S</i>	Entropy
<i>T</i>	Absolute temperature
<i>V</i>	Volume

### *Lower Case:*

<i>a</i>	Activity
<i>f</i>	Fugacity
<i>p</i>	Partial pressure (in gas mixture)
<i>x</i>	Mol fraction in liquid phase
<i>y</i>	Mol fraction in vapor phase

### *Subscripts:*

<i>a, b, c, d</i>	Components in mixture
<i>C</i>	Concentration
<i>H</i>	Constant enthalpy
<i>M</i>	Molal
<i>P, p</i>	Constant pressure
<i>S</i>	Constant entropy

$T$	Constant temperature
$T, v$	Constant volume

*Superscripts:*

<sup>0</sup>	Standard state
*	Refers to perfect-gas region

*Greek Letters:*

$\alpha, \beta, \gamma$	Constants in Equation 22
$\Delta$	Value in final state — Value in initial state
$\pi$	Total pressure
$\mu$	Gas compressibility factor, $PV/NRT$
$\mu$	Joule-Thomson coefficient, $(\partial T/\partial P)_H$ , Equation 6

## PROBLEMS

1. Referring to Problem 3, Chapter XVI, calculate the value of  $K_a$  at 300 atm. and 300°C. For  $\text{NH}_3$ :  $C_p = 6.70 + (6.30)(10^{-3})(T^\circ\text{K.})$ .

2. Construct a plot or series of plots for estimating the entropy of pentane at any pressure or temperature.

1. Pentane may be assumed to follow the  $\mu$ -chart.

2. At  $P = 0$  atm.,  $C_p^*/M = 0.362 + 0.00060 T^\circ\text{F.}$

3. Using the  $\mu$ -chart, explain how you would get the work of reversible adiabatic expansion of a pure gaseous hydrocarbon.

4. Show that for a gas following the relation

$$PV = NRT$$

the internal energy must be a function of temperature only.

5. Parks and Huffman give for the formation of ethylene from the elements at temperatures between 400°K. and 1000°K.:  $2\text{C (graphite)} + 2\text{H}_2\text{g} = \text{C}_2\text{H}_4\text{g}$ ;  $\Delta F^0 = 5700 + 21.1 T^\circ\text{K.}$  Do you consider the industrial preparation of ethylene according to this reaction feasible? Justify your conclusions by thermodynamic calculations.

6. Under what conditions will the free energy change for a chemical reaction be independent of temperature?

7. Under what conditions will the free energy change for a chemical reaction be independent of pressure?

8. A boiler feed pump takes water at 700°C. and 3206.2 lb. sq. in. abs. and delivers into a digester where the pressure is 5000 lb./sq. in. abs. Assuming isothermal operation, estimate, from experimentally determinable quantities to be found in the steam tables, the entropy change of the water in passing through the pump.

9. For many gases under conditions not too close to the critical, the isometrics are practically straight. Assuming that the equation for any isometric is

$$P = RTf_1(V) - f_2(V)$$

derive, with the aid of the Maxwell relations, expressions for  $\Delta S$ ,  $\Delta F$ , and  $\Delta H$ .

## CHAPTER XVIII

### PARTIAL MOLAL QUANTITIES

Systems containing one or more liquid solutions are of frequent occurrence in engineering work. Certain conventions, more particularly the partial molal concept, are helpful in the thermodynamic analysis of these, especially in determining the effect of changing concentrations. Obviously the ideas to be presented in this section are supplementary to the more general relations previously presented.

**The Partial Molal Concept.** Consider any extensive property of a solution, such as the internal energy, the volume, the enthalpy, or the total free energy, to be definite, the internal energy. Assume the system composed of only two components, perhaps a simple ammonia-water solution at fixed temperature and pressure.

It is instructive to review a few of the possible ways of producing the solution. In each case pure ammonia gas and pure liquid water will be used as raw materials, and for simplicity it may be assumed that the final solution contains only ammonia molecules and water molecules. All operations will be carried out isothermally and at constant total pressure. In making the solution  $N_1$  mols of ammonia will be used and  $N_2$  mols of water.

1. The ammonia may be added to the water or conceivably the water to the ammonia until a specified quantity of solution is produced. After formation the internal energy of the system will be  $E$ , irrespective of which substance is added to the other. This simple method of making the solution is not particularly interesting.

2. Both the water and the ammonia may be added simultaneously to the solution container each at any arbitrarily chosen rate. When the solution has been formed its internal energy will be  $E$  as in the previous case. The mathematician could set up an equation to explain this operation in terms of the relative amounts of the two substances used. This could be of the form:

$$dE = \frac{\partial E}{\partial N_1} dN_1 + \frac{\partial E}{\partial N_2} dN_2 \quad (1)$$

3. A third method of producing the solution comes to mind. This may be thought of as a special case of the second method described. The ammonia and water will be added simultaneously to the final

container but always at such constant rates that from the first differential quantity of solution formed all will be of the desired final concentration. This is an accepted method of carrying out certain chemical reactions such as precipitations when all products must be formed under similar conditions.

Although the mathematician might use Equation 1 to express the third method, he would no doubt also write<sup>1</sup>

$$E = \bar{E}_1 N_1 + \bar{E}_2 N_2 \quad (2)$$

As in the other two cases  $E$  is the internal energy of the final solution while  $\bar{E}_1$  and  $\bar{E}_2$  are internal energies per mol of ammonia and water added, so chosen that, when multiplied by  $N_1$  and  $N_2$ , the sum of the products gives  $E$ .  $\bar{E}_1$  and  $\bar{E}_2$  are not to be thought of as average values, but as fixed quantities dependent on concentration though not on the quantity of solution. Mathematically, Equation 2 is an integration of Equation 1, with  $\frac{\partial E}{\partial N_1}$  and  $\frac{\partial E}{\partial N_2}$  constants, a limitation allowable because the components were added at constant rates. It is well to remember that  $\bar{E}_1$  and  $\bar{E}_2$  are not the energies per mol of original ammonia or per mol of original water. This would be true only were there no energy changes on mixing.

In Equation 1 the coefficients  $\frac{\partial E}{\partial N_1}$  and  $\frac{\partial E}{\partial N_2}$  may be visualized as the change in internal energy of an infinite amount of solution as one mol of either ammonia or water is added, or, if it is easier, as the differential change in internal energy of a finite amount of solution when a differential amount of either ammonia or water is added. As the concentration changes, these differential coefficients will vary and in fact over wide limits.

But reference to Equation 2 shows that the ratios expressed by  $\bar{E}_1$  and  $\bar{E}_2$  are also the changes in internal energy (of a quantity of solution as one mol of either ammonia or water is added to an infinite amount of solution, or as a differential amount of either material is added to a finite amount. In this respect, they are coefficients of the same type as those in Equation 1 with the exception that they are representative of conditions (constant because of the way the solution was formed) existing in the final solution rather than changing conditions at intermediate concentrations.

<sup>1</sup> For a more complete mathematical discussion refer to Euler's theorem on homogeneous functions in any suitable textbook such as Mellor's "Higher Mathematics for Students of Chemistry and Physics," p. 75.

At any chosen concentration, for a differential amount of solution formed, there is no real distinction between the coefficients in Equations 1 and 2. All are of the general form:

$$\left(\frac{\partial E}{\partial N_1}\right)_{P,T,C} \quad \text{or} \quad \left(\frac{\partial E}{\partial N_2}\right)_{P,T,C}$$

It will be convenient to have names for these. They are called *partial molal quantities* — partial because, as in any partial differential, but one variable is changing; molal because they are on a molal basis. For brevity the appropriate function surmounted by a bar will denote these quantities, e.g.,

$$\left(\frac{\partial E}{\partial N_1}\right)_{P,T,N_2} = \bar{E}_1; \quad \text{or} \quad \left(\frac{\partial E}{\partial N_2}\right)_{P,T,N_1} = \bar{E}_2$$

Strictly by mathematical manipulation, a third fundamental and useful equation may be derived. Referring to Equation 2, this may be differentiated:

$$dE = N_1 d\bar{E}_1 + \bar{E}_1 dN_1 + N_2 d\bar{E}_2 + \bar{E}_2 dN_2 \quad (3)$$

But Equation 1 may also be written

$$dE = \bar{E}_1 dN_1 + \bar{E}_2 dN_2 \quad (4)$$

Equating 3 and 4

$$N_1 d\bar{E}_1 + N_2 d\bar{E}_2 = 0 \quad (5)$$

Reconsidering the discussion of the past few pages will serve to emphasize certain important conclusions.

1. The argument would have been entirely similar for a solution of any number of constituents.
2. The change of any extensive property of the solution with respect to the number of mols of a chosen constituent, all other variables remaining constant, is a partial molal quantity.
3. The partial molal quantities are true intensive (phase rule) variables. They are point functions.
4. If the mol fraction of any solution constituent is defined as

$$x_1 = \frac{N_1}{N_1 + N_2 + \dots}$$

equations similar to the above but containing in every case  $x$  instead of  $N$  will result.



5. Various equations involving extensive properties such as

$$F = H - TS \quad \text{and} \quad A = E - TS$$

may be written in terms of partial molal quantities. Thus differentiating the above equations with respect to change in number of mols of the first constituent  $N_1$ , the pressure, temperature, and mols of other constituents remaining constant,

$$\frac{\partial F}{\partial N_1} = \frac{\partial H}{\partial N_1} - T \frac{\partial S}{\partial N_1} \quad \text{and} \quad \frac{\partial A}{\partial N_1} = \frac{\partial E}{\partial N_1} - T \frac{\partial S}{\partial N_1}$$

$$\bar{f}_1 = \bar{H}_1 - T\bar{S}_1 \quad \text{and} \quad \bar{A}_1 = \bar{E}_1 - T\bar{S}_1$$

**Utility of Partial Molal Concept.** Of the partial molal functions, probably the free energy is the most useful. According to Equation 2 the total free energy of a solution is given by

$$F = \bar{F}_1 N_1 + \bar{F}_2 N_2 + \dots \quad (6)$$

In such an expression,  $\bar{F}_1$ ,  $\bar{F}_2$ , etc., have the characteristics of potentials and may well be considered as such. Ardent followers of J. Willard Gibbs will recognize  $\bar{F}$  as his  $\mu$ .

Equation 6 may be compared with a somewhat similar equation for one mol of a perfect-gas mixture.

$$P = p_1 N_1 + p_2 N_2 + \dots \quad (7)$$

In this case the partial pressures  $p_1$ ,  $p_2$ , etc., are potentials. For equilibrium between two perfect-gas mixtures, at the same temperature, it is necessary that the partial pressures of each and every component be the same in each. There is no exact counterpart of Equation 7 in terms of fugacity for imperfect gas mixtures. However for these the fugacity of every component must be the same in every phase for equilibrium to prevail.

In the light of the previous discussion it is consistent to define the fugacity of any *constituent of a solution, mixture, or other complex* by the equation

$$\bar{F}_1 = RT \ln f_1 + C_T \quad (8)$$

where  $C_T$  is a constant at a given temperature. Moreover, the change in partial molal free energy for any constituent as the complex passes isothermally from any initial to any final state is

$$\Delta \bar{F}_1 = RT \ln \frac{f_2}{f_1} \quad (8a)$$

For equilibrium between phases at the same temperature it is necessary that the partial molal free energy of any constituent be the same in all phases. Therefore the fugacity (and the activity, relative fugacity) must be the same for any chosen constituent in each phase. The partial molal free energy of a constituent of a mixture is equal to the molal free energy of that component in a pure state at the same temperature as the mixture and under a pressure equal to its equilibrium pressure as it exists in the mixture. These partial molal free energies are the chemical potentials previously referred to in Chapter III.

**Fugacities of Components in Gas Mixtures.** Methods for determining the fugacities for components of gaseous mixtures from the fugacities of the components when in a pure state at the same temperature would be extremely useful. Although in general this cannot be done often the empirical relation<sup>1</sup>

$$f = f_{\pi} y_a \quad (8b)$$

is assumed where  $f_a$  equals the fugacity of component  $a$  in the mixture;  $f_{\pi a}$  its fugacity at the temperature and total pressure of the mixture; and  $y_a$  the mol fraction of  $a$  in the mixture. With the aid of the fugacity chart  $f_a$  may be found for each constituent.<sup>2</sup> With fugacities at the initial and final states for each substance known,  $\Delta \bar{F}$  is calculated using Equation 8a. After  $\Delta \bar{F}$  for each constituent is thus calculated it is assumed that  $\Delta F_{\text{mixture}} = \sum N \Delta \bar{F}$ . Near the critical region, this method is seriously in error.

**Approximate Method of Calculating Vapor Liquid Equilibria for Mixtures.** For a gaseous mixture in equilibrium with the liquid from which it is evolved, in addition to Equation 8b it is often assumed that for each component in the liquid

$$f_a = f_p x \quad (8c)$$

In this equation  $f_a$  is the fugacity of component  $a$  in the liquid and  $f_p$  its fugacity at the temperature of the mixture and at a pressure corresponding to the vapor pressure of pure liquid  $a$  at this temperature. Since equilibrium prevails, for each component

$$f_{\pi} y = f_p x$$

and for the system as a whole

$$\sum x = 1; \quad \sum y = 1$$

<sup>1</sup> Lewis and Randall, *op. cit.*, pp. 225-227.

<sup>2</sup> The procedure suggested by Equation 8b may lead to considerable error when applied to a constituent of a mixture if the mixture pressure is above the vapor pressure of the pure constituent. Moreover, the results obtained by this procedure are in error for a substance above the critical. This is unfortunate because the applicability of this simple method is thereby seriously limited.

These assumptions make possible the approximate solution of many problems met in work where vaporization of a complex mixture occurs.

The dotted lines on Figure 1, Chapter XV, were obtained from experimental vapor-liquid equilibrium data and the assumption that Equation 8d was valid.

For convenience in calculation it is sometimes desirable to have available tables of  $y/x$  or  $f_p/f_\pi$  versus pressure at various temperatures. For some of the hydrocarbons Sherwood<sup>1</sup> has tabulated these. The ratio  $y/x$  is often called an equilibrium constant and is usually indicated by the symbol  $K$ .

**Effects of Pressure, Temperature, and Concentration on Partial Molal Quantities.** The effects of pressure and temperature are readily found by analogy with the general expressions previously derived for the various important functions. For the free energy;

$$\left(\frac{\partial \bar{F}_1}{\partial P}\right) = \bar{V}_1$$

$$\left(\frac{\partial \bar{F}_1}{\partial T}\right) = -\bar{S}_1 = \frac{\bar{F}_1 - \bar{H}_1}{T}$$

Since  $\bar{F}_1 = RT \ln f_1 + C_T$

$$\left(\frac{\partial \ln f_1}{\partial P}\right)_T = \frac{\bar{V}_1}{RT}$$

$$\left(\frac{\partial \ln f_1}{\partial T}\right)_P = \frac{H_{M,1}^* - \bar{H}_1}{RT}$$

While, for the system as a whole, in view of Equation 2

$$N_1 \left(\frac{\partial \ln f_1}{\partial P}\right) + N_2 \left(\frac{\partial \ln f_2}{\partial P}\right) + \cdots = \frac{V}{RT} \quad (9)$$

$$N_1 \left(\frac{\partial \ln f_1}{\partial T}\right) + N_2 \left(\frac{\partial \ln f_2}{\partial T}\right) + \cdots = \frac{H^* - H}{RT^2} \quad (10)$$

A mathematical expression for the effect of changing the amount of any of the constituents of a solution is readily obtained from an equation similar to (5),

$$N_1 \frac{\partial \bar{F}_1}{\partial N_1} + N_2 \frac{\partial \bar{F}_2}{\partial N_1} + \cdots = 0 \quad (11)$$

*Binary Mixtures.* Applying an equation similar to (11) to a two-component solution gives

$$\frac{\partial \bar{F}_1}{\partial \bar{F}_2} = - \frac{N_2}{N_1}$$

or

$$\frac{\partial \ln f_1}{\partial \ln f_2} = - \frac{N_2}{N_1}$$

If the equilibrium vapors arising from the solution follow the gas laws, partial pressures may be substituted for fugacities.

$$\frac{\partial \ln p_1}{\partial \ln p_2} = - \frac{N_2}{N_1} \quad (13)$$

If  $x$  is the mol fraction of the first component,  $(1 - x)$  is that of the second and

$$\frac{\partial \ln p_1}{\partial \ln p_2} = \frac{x - 1}{x} \quad (14)$$

Equation 13 or 14 is usually called the Duhem equation.<sup>1</sup> It is a necessary relation between the partial pressures of the components of any binary mixture, the vapors of which follow the gas laws. Integrating equations of the Duhem type is often difficult and in all cases necessitates a knowledge of partial pressures as a function of composition.

The Duhem equation may be obtained by a somewhat different method. Assume any binary solution the vapors from which follow the gas laws. The free energy increase on separating such a solution into its constituents is

$$\Delta F = N_a RT \ln \frac{P_a}{p_a} + N_b RT \ln \frac{P_b}{p_b} \quad (15)$$

where  $p_a$ ,  $p_b$  are partial pressures of constituents in solution and  $P_a$ ,  $P_b$  are vapor pressures of pure  $a$  and  $b$ .

But in addition

$$\Delta F = \int_0^N RT \ln \frac{P_a}{p_a} dN_a \quad (16)$$

Equating 15 to 16, canceling common factors, and differentiating the result with respect to  $N_a$ , holding  $N_b$  constant,

$$\ln \frac{P_a}{p_a} - N_a d \ln p_a - N_b d \ln p_b = \ln \frac{P_a}{p_a}$$

This reduces to

$$\frac{d \ln p_a}{d \ln p_b} = - \frac{N_b}{N_a}$$

<sup>1</sup> Duhem, *Compt. rend.*, 102, 1449 (1886).

**Determination of Partial Molal Quantities.** Three general methods for evaluating these quantities may be suggested.

1. If the desired extensive property of the system is known as a function of the amounts of the various constituents and this relation is expressed in the form of an algebraic equation, simple partial differentiation of this will immediately yield the desired partial molal quantities.

2. If the available data can be more conveniently expressed as a graph in which values of the chosen extensive variables are plotted as ordinates, while the mols,  $N_1$ , of any desired constituent are plotted as abscissas, the mols of all other constituents being held constant, at any chosen value of  $N_1$ , the slope of the curve is the desired partial molal quantity. Curves for actual mixtures indicate that the partial molal quantities may be positive, negative, or infinite in value.

3. A third method applicable to binary mixtures has been suggested by Roozeboom.<sup>1</sup> If a plot is made of molal enthalpy for a solution (*i.e.*, enthalpy per mol of total solution) as ordinate and mol fraction as abscissa and a tangent is drawn to the resulting curve at any chosen point, the intercept of this tangent at  $x_1 = 1$  gives directly  $\bar{H}_1$  while its intercept at  $x_2$  gives  $\bar{H}_2$ . The same method may be used to evaluate the other partial molal quantities.

### SUMMARY

1. The change of any extensive variable of a system with respect to the number of mols of a chosen component, temperature, pressure, and mols of other constituents remaining constant, is known as a partial molal quantity, *e.g.*,  $(\partial H / \partial N_1)_{T, P, N_2, \text{etc.}} = \bar{H}_1$ . The concept is especially useful in dealing with solutions since the familiar equations in terms of total quantities as applied to the system as a whole may be used unchanged in form for each constituent. Thus for the whole  $F = H - TS$ , while for the component arbitrarily designated as the first

$$\bar{F}_1 = \bar{H}_1 - T\bar{S}_1$$

2. Three important equations connect these quantities

$$E = \bar{E}_1 N_1 + \bar{E}_2 N_2 + \cdots \quad 2$$

$$dE = \bar{E}_1 dN_1 + \bar{E}_2 dN_2 + \cdots \quad 4$$

$$N_1 d\bar{E}_1 + N_2 d\bar{E}_2 + \cdots = 0 \quad 5$$

3. The partial molal free energy is the real measure of chemical potential for any constituent of a system.

<sup>1</sup> "Die heterogenen Gleichgewichte," II-1, p. 288, Braunschweig, 1904; and see Lewis and Randall, "Thermodynamics," p. 38, for a simple geometric proof.

4. All partial molal quantities are true intensive (phase-rule) variables. Moreover, they are point functions.

5. Their evaluation is readily carried out from the appropriate experimental measurements by one or more of the three methods outlined.

### NOTATION FOR CHAPTER XVIII

#### *Upper Case:*

$C$	A constant
$E$	Internal energy
$F$	Free energy
$H$	Enthalpy
$N$	Number of mols
$P$	Absolute pressure
$R$	Gas constant
$S$	Entropy
$T$	Absolute temperature
$V$	Volume

#### *Lower Case:*

	Activity
$f$	Fugacity
$p$	Partial pressure
	Mol fraction in the liquid phase
	Mol fraction in the vapor phase

#### *Subscripts:*

$C$	Constant concentration
$M$	Molal
$N$	Constant mols
$P$	Constant pressure
$T$	Constant temperature
$a, b, 1, 2, 3$	Constituents in mixture
$\pi$	Total pressure of mixture

#### *Special:*

$\bar{\phantom{x}}$	Denotes partial molal quantity, as $\bar{E}_1 = \frac{\partial E}{\partial N_1}$
*	Refers to perfect-gas region
$\Sigma$	A summation of quantities

### PROBLEMS

1. Referring to Problem 7, Chapter X, calculate, for a solution containing 50 gm. of ammonia per 1000 gm. of water, the partial molal free energies for the two solution constituents.

2. Referring to Problem 6, Chapter X, what is the partial molal free energy of the solute in a solution containing 17.05 gm. of NaCl for 100 gm. of water? What is the partial molal volume of the NaCl in this solution?

3. Prove that if Raoult's law applies over a given range for one constituent of a binary mixture, over the same range Henry's law must hold for the other.

4. A tower is to be constructed for drying air at  $68^{\circ}\text{F}$ . with 90 per cent (by weight) sulfuric acid. The acid after leaving the base of the tower will be reconcentrated, cooled to  $68^{\circ}\text{F}$ ., and returned to the top of the drying tower. The quantity of acid circulated is so large relative to the amount of air dried that the acid concentration does not change materially as it passes through the tower. If the tower operates isothermally, how much heat must be lost from the tower per 100 lb. of water removed from the air?

5. A 50 mol per cent mixture of pentane and hexane at  $100^{\circ}\text{C}$ . is found to be just 50 per cent vapor on a molal basis. Under what pressure is the mixture?

6. A mixture containing 30 mol per cent propane, 50 mol per cent butane, and 20 mol per cent hexane originally at 1 atm. and  $120^{\circ}\text{C}$ . is compressed isothermally to a point where condensation occurs.

(a) What is the final pressure of the mixture?

(b) What is the composition (mol fraction) of the first drop condensing?

(c) If the compression is carried out reversibly, what is the work required per 100 mols of mixture handled?

7. Construct the loop curve (a plot of  $P$  versus  $T$  at constant composition) for a mixture containing 77 mol per cent ethane and 23 mol per cent heptane. On this plot, locate the curve corresponding to 50 mol per cent vaporized.

## CHAPTER XIX

### ELECTROCHEMICAL EFFECTS

To interpret properly the overall results of energy changes in systems containing solutions of electrolytes requires no ideas or concepts not previously presented. However, because the generally accepted idea that many of the characteristics of such solutions are due to the presence of ions is so widespread and so completely a part of present-day chemistry, it is desirable to interpret once more at least the more important findings of thermodynamics in these terms. To a certain extent this is inquiring into the mechanism of the change taking place, a task with which we have not often concerned ourselves. The field to be considered in this chapter, however, is of sufficient importance to the engineer to warrant a more detailed treatment than is possible from the application of the general relations already presented.

In spite of the great amount of work which has been done, the results fall short of what is desired, from an engineering viewpoint. Except in dilute solutions, methods of correlation have not been widely developed. Moreover, especially among early workers, a considerable amount of data was collected on cells in which, owing to impurities and side reactions, the actual changes giving rise to the measured effects were not exactly known.

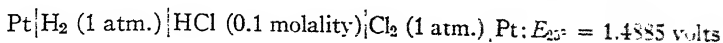
Since in some respects a study of electrolytes does constitute a specialized branch of thermodynamics, it is reasonable to expect that workers in this field will have developed a language particularly applicable to their needs. Much of this will already have been presented to students of physical chemistry, but it seems worth while to review at this point. The next several pages may be looked upon as a brief glossary of the more important terms and ideas associated with the thermodynamics of electrolytes.

**Fundamental Considerations and Conventions.** If two phases, differing in any respect, are brought into contact an electrical potential may result. Discussion will be limited to those changes where a simple reaction may be considered as occurring and more especially to systems including at least one liquid phase.

A series of dissimilar phases in contact and so arranged that electrical energy resulting from a chemical change may be withdrawn constitutes a cell or some-

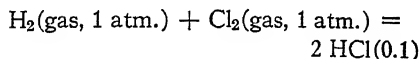


times a series of cells. To represent the conditions and chemical changes it is customary to use symbols. Thus for the cell illustrated in Figure 1,

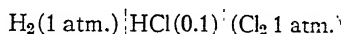


In this expression the various phases are placed in the order in which they are in contact. The exact condition of each is either indicated or understood from the surrounding conditions. Each phase boundary is shown by a vertical bar. The concentration of HCl (0.1 molality) unless otherwise stated is on a basis of mols of solute per kilogram of solvent.

The change in state taking place, if the two platinum strips are connected and two faradays of electricity passed through the cell, is:



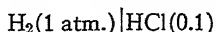
In this, as in any cell, the exact process taking place must be clearly formulated. In describing this cell one would say that it consisted of a hydrogen electrode, a chlorine electrode, and an electrolyte of 0.1 molal hydrochloric acid. Unless otherwise stated the electrolyte is an aqueous solution. As far as any reaction is concerned the platinum is inert and may be ignored. It is merely a convenient means for making electrical connection. The change taking place, the cell reaction, might also have been indicated by the expression



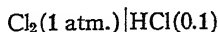
It is common practice to designate as anode that electrode at which oxidation (valence increase) takes place, while at the cathode reduction occurs. Here the hydrogen electrode is the anode, the chlorine electrode the cathode.

In any cell the electricity enters and leaves at the electrodes, the electrolytes serving to carry electricity by means of charged particles of matter, ions. When the two electrodes are connected to an external circuit, all electricity flowing must also pass through the cell.

Often a single cell is discussed as though it consisted of merely two electrodes. In the cell just mentioned the anode might be described as



and the cathode as



Each of these could also be called a half cell. The total voltage in this case would be the sum of the voltages of the two half cells.

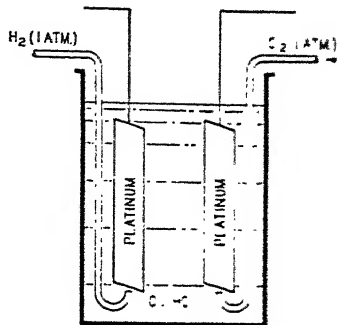
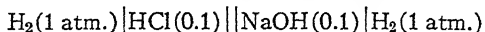


FIG. 1. Cell with Hydrogen and Chlorine Electrodes.

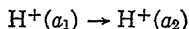
**Sign of the Electromotive Force.** A positive sign for the potential developed by the whole cell indicates that the reaction as written tends to go from left to right, and, if an external circuit is attached to the cell, work as electricity may be withdrawn. Furthermore, a positive sign indicates that the left electrode is the anode.

**Liquid Junctions.** Cells are often set up in which there are one or more junctions between liquid phases. In the cell indicated by



there is a liquid junction between the HCl and the NaOH phases. This is a source of small but uncertain potential, and, although up to moderate concentrations this potential may be estimated, in general its exact determination is difficult. The liquid junction potential is that due to effects other than the difference in activities of the hydrogen ions in the two liquid phases. It is often assumed that junction potentials may be eliminated by means of a bridging conductor composed of a saturated solution of certain salts (usually KCl). This procedure may minimize the effect, but certainly elimination of the undesired potentials is not complete in most cases. The symbol  $||$  means that some method has been adopted to correct for liquid junction potential and the voltage recorded is that the cell is supposed to have in the absence of such.

**Process Causing the Potential.** The cell just mentioned deserves additional comment. The reaction under measurement here is hydrogen ion at the activity  $a_1$  it has in a 0.1 molal HCl solution being transferred to a solution 0.1 molal in NaOH, where its activity is  $a_2$  or in general

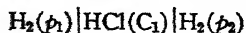


It is the potential caused by this reaction which is measured in a properly arranged cell. It is assumed that the only ion effective for causing a potential is the hydrogen ion. The sodium, chlorine, and hydroxide ions are assumed inert in this respect. In such cells extreme care must be exercised that no impurities which can react with the electrodes (hydrogen) are present. Thus a small amount of oxygen in the hydrogen used to form the hydrogen electrodes may introduce serious errors; likewise, certain oxidizing materials as impurities in the solution are to be avoided.

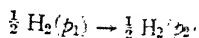
In any cell the exact process causing the voltage must be formulated. Reaction at the interface between HCl and NaOH is not accompanied by an electrode reaction and, except as interaction may change concentrations, will have no effect on the measured potential. To minimize this secondary effect some construction such as a small capillary or an imperfectly fitted ground-glass joint is often used as a connection between the half cells. Neutralization is then limited to a small area between the two.

**Types of Cells.** Cells may be classified according to the changes in state occurring in them when a current is passed.

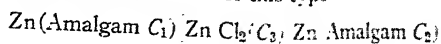
**Cells Involving Simple Physical Changes.** An example of this type is



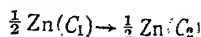
The reaction is oxidation of hydrogen gas originally at a pressure  $p_1$  to form hydrogen ion (at the anode) and the simultaneous reduction of hydrogen ions to yield hydrogen gas (at the cathode) at a pressure  $p_2$ . For one faraday of electricity passed the change is



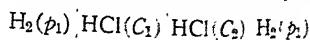
Amalgam cells are also representative of this type



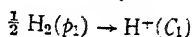
For one faraday passed the change is



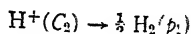
**Concentration Cells with Transport.** These are so named because the change occurring is the transfer of a given amount of material from a solution of one concentration to a second differing from the first only in concentration.



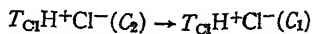
At the anode the reaction, for one faraday, is



At the cathode

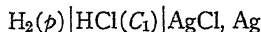


Through the electrolyte both hydrogen and chloride ions act as carriers of electricity, and each kind of ion is transferred in amount proportional to the quantity of electricity it carries, *i.e.*, in proportion to its transference number. Let  $T_{\text{H}}$  be the transference number for the hydrogen ions while  $T_{\text{Cl}}$  is that for chloride ions. By transference,  $T_{\text{Cl}}$  equivalents of chloride ion move from right to left while  $T_{\text{H}}$  equivalents of hydrogen ion move from left to right. The anode (left) half of the cell gains  $T_{\text{Cl}}$  equivalents of chloride ion and loses  $T_{\text{H}}$  equivalents of hydrogen ion or a gain of  $(T_{\text{Cl}} - T_{\text{H}})$  equivalents of both kinds of ions, because of transference alone. Similarly the cathode half of the cell loses  $T_{\text{Cl}}$  equivalents of chloride ion and gains  $T_{\text{H}}$  equivalents of hydrogen ion, a loss of  $(T_{\text{Cl}} - T_{\text{H}})$  equivalents by transference. Moreover, since all the current must be carried either by hydrogen or chloride ions,  $T_{\text{Cl}} + T_{\text{H}} = 1$ . But, owing to electrolysis at the electrodes, one equivalent of hydrogen ion has been added to the anode side, making a net gain due to all effects of  $T_{\text{Cl}}$  equivalents of hydrogen ion and  $T_{\text{Cl}}$  equivalents of chloride ion. Similarly the cathode side has lost  $T_{\text{Cl}}$  equivalents of hydrogen ion and  $T_{\text{Cl}}$  equivalents of chloride ion. The whole process is equivalent to transferring  $T_{\text{Cl}}$  equivalents of hydrochloric acid from a solution where its concentration is  $C_2$  to one where its concentration is  $C_1$ :

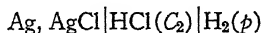


**Concentration Cells without Transport.** If two cells are set up in which the only difference is the concentration of the electrolyte and then these cells are connected to oppose each other, on the passage of electricity the process occur-

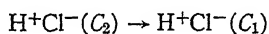
ring is equivalent to the transfer of material from one electrolyte to the other. For example, the two cells might be



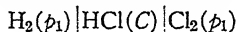
and



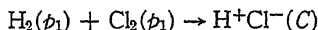
If these two cells are connected with the two silver chloride electrodes together, a cell without transport is formed and the net effect of allowing a faraday of electricity to flow is equivalent to transfer of one equivalent of hydrochloric acid from the second cell where its concentration is  $C_2$  to the first where its concentration is  $C_1$ :



**Chemical Cells.** In these the process is a chemical reaction. In the cell



the reaction is



**Reversibility in Cells.** Certainly, as far as the development of thermodynamic relations is concerned, measurements on cells operating reversibly are of primary importance. The same criteria as used previously are applicable here. To minimize such irreversible effects as voltage drop through the cell itself, changes in concentration due to passage of electricity, and overvoltage effects at electrodes, observations must be made under conditions of very small current flow. One method of attaining this is to balance the cell voltage by an externally applied opposing voltage as in the potentiometric method. By using sensitive galvanometers to indicate a condition of balance, results satisfactory for even precise work may be obtained. Moreover, the type of cell must be carefully selected to ensure not only that the voltage set up is that due to the supposed reaction and no other, but also that with the cell voltage balanced by an external potential chemical reaction is eliminated.

**Reproducibility of Cells and Electrodes.** Not only must the cell operate reversibly, but in addition different investigators using cells similarly constructed should be able to duplicate results. To this end at least the standard cells should be easily reproducible. The Weston cell fulfills this requirement better than practically any other and in addition has a comparatively small voltage coefficient with temperature. This is a satisfactory standard of potential with which to compare others but is useless for directly investigating chemical reactions other than its own. As a matter of fact, it is rather difficult to devise satisfactory cells for many reactions.

**Standard Electrodes.** For purposes of comparison it is desirable to have standard electrodes or half cells. Two of importance are the hydrogen and the calomel electrodes. The first may be a strip of platinum, often coated with platinum black, over the surface of which is bubbled pure hydrogen gas at 1 atm. pressure. The strip is immersed in a solution having a concentration of hydrogen ions such that their activity is unity. The platinum is inert and is supposed to be covered with a film of hydrogen gas, this forming the true active surface.

The calomel electrode is mercury covered with a layer of sparingly soluble mercurous chloride (calomel), the whole surmounted by a solution of potassium chloride saturated with calomel. The potassium chloride layer may be either saturated or tenth normal in potassium chloride. By combining a standard hydrogen and a standard calomel electrode a cell is formed the reversible voltage of which may be measured. But there is no way to determine the absolute potential of either electrode alone. In view of this it is assumed that at any temperature the voltage of the standard hydrogen electrode is zero. With such an assumption the voltage of a cell made up of a hydrogen and calomel electrode is the voltage of the calomel electrode alone. At 25°C. the voltage of the saturated calomel electrode is  $-0.270$ , while that of the tenth normal is  $-0.333$ .

**The Electromotive Series.** From the preceding discussion it is clear that each chemical element in contact with an aqueous solution one normal in its ion could in turn be compared with the standard hydrogen electrode. In this way the familiar electromotive series of the elements may be established, Table I. It is of value in industrial electrolytic work to indicate which of several ions will deposit first, provided that proper correction is made for concentration, overvoltage, and related effects.

**Thermodynamic Considerations.** Theoretically at least, changes in state may be visualized as carried out isothermally and reversibly in a cell yielding or requiring a net work effect, the free energy change for the reaction, entirely as electrical work. A familiar example is the electrolysis of water to yield oxygen and hydrogen each at 1 atm. This reaction carried out reversibly and isothermally at 25°C. requires 54,507 calories of electrical work per gram mol of hydrogen (and per half gram mol of oxygen produced). Exactly the same amount might be recovered as mechanical work by allowing the oxygen and hydrogen to reunite reversibly and isothermally to form water. To do this the mechanical process could be visualized as carried out in engines expanding the gases from 1 atm. to their very small partial (equilibrium) pressures over water at 25°C. and then causing them to combine, forming water in an equilibrium box without net work effect.

Granting the preceding argument, one is forced to admit that, in all the equations involving free energy previously derived, net isothermal

TABLE I  
ELECTRODE POTENTIALS AT 25°C.\*

Reaction	Volts
$\text{Li} = \text{Li}^+ + e \dots$	2.960
$\text{K} = \text{K}^+ + e \dots$	2.924
$\text{Na} = \text{Na}^+ + e \dots$	2.716
$\frac{1}{2}\text{H}_2 + \text{OH}^- =$	0.830
$\text{Zn} = \text{Zn}^{++} + 2e \dots$	0.762
Cr	0.56
Fe	0.44
Cd	0.401
Ni	0.23
$\text{Sn} = \text{Sn}^{++} + 2e \dots \dots \dots$	0.14
$\frac{1}{2}\text{H}_2 = \text{H}^+ + e \dots \dots \dots$	0.000
Normal calomel electrode	-0.281
0.1 <i>N</i> calomel electrode...	-0.333
$\text{Cu} = \text{Cu}^{++} + 2e \dots \dots \dots$	-0.344
$\text{Fe}^{++} = \text{Fe}^{+++} + e \dots \dots \dots$	-0.748
$\text{Ag} = \text{Ag}^+ + e \dots \dots \dots$	-0.798
$\text{Sn}^{++} = \text{Sn}^{++++} + 2e \dots \dots$	-1.256
$\text{Cl}^- = \frac{1}{2}\text{Cl}_2 + e \dots \dots \dots$	-1.358

\* "International Critical Tables," Vol. 6, p. 332.

reversible electrical work might have been substituted for the more general free energy. This offers no complication.

One of the few fundamental laws to which there seems to be no exception is that of Faraday, in which it is stated that to deposit one gram equivalent of any material at either electrode of a cell requires the passage of a quantity of electricity equal to 96,494 coulombs. This experimentally determined fact has been repeatedly verified. If the reversible potential under which deposition takes place is  $E$ , the reversible electrical work is

$$W_e = ENF = -\Delta F$$

where

$E$  = reversible voltage of cell

$N$  = gram equivalents of material deposited at *either* electrode

$F$  = 1 faraday = 96,494 coulombs

A summary of a few important relations expressed in terms of voltage is given in Table II.

TABLE II

General	In Terms of E
(1) $\frac{\Delta F - \Delta H}{T} = \frac{d(\Delta F)}{dT}$	$\frac{ENF + \Delta H}{T} = NF \frac{dE}{dT}$
	$E + \frac{\Delta H}{NF} = T \frac{dE}{dT}$
(2) $\Delta F = RT \ln \frac{a_2}{a_1}$	$E = \frac{-RT}{NF} \ln \frac{a_2}{a_1}$
	$= \frac{-RT}{NF} \ln \frac{\gamma_2 C_2}{\gamma_1 C_1}$
(3) $\Delta F^0 = -RT \ln K_a$	$E^0 = \frac{RT}{NF} \ln K_a$
(4) $\Delta F = \Delta F^0 + RT \ln K'_a$	$E = E^0 - \frac{RT}{NF} \ln K'_a$

In conformity with the custom of dividing the whole cell into two electrodes the free energy effect for the chemical reaction at each electrode is often discussed. If these are the only sources of potential,

$$\Delta F = \Delta F_{\text{anode}} + \Delta F_{\text{cathode}}$$

or

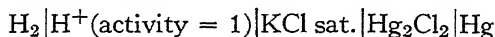
$$E = E_{\text{anode}} - E_{\text{cathode}}$$

**Tabulation of Data.** Two common methods are in use for tabulating equilibrium data. For chemical reactions in general, it is more convenient to list values of  $K$ , the equilibrium constants, or the standard free energies,  $\Delta F^0$ . For many of the less complex processes, which may be readily visualized as taking place in simple cells, tables of electrode potentials offer advantages.

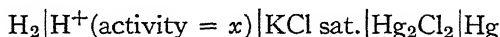
**Electrometric Determination of pH.** A practical and important application of Equation 2 is found in the many commercially available devices for determining hydrogen-ion concentration. These are often cells containing a standard calomel electrode and a hydrogen or some similar electrode (such as a quinhydrone or glass electrode) around which is placed the solution of unknown hydrogen-ion concentration. The apparatus usually contains a standard cell for comparison purposes and sufficient auxiliary apparatus to make possible voltage readings under substantially reversible conditions. Many modern instruments include some type of vacuum-tube circuit. These offer the possibili

of measuring voltage under conditions of extremely small current flow.

Since the value of the standard hydrogen electrode is arbitrarily assumed zero, the voltage of the calomel electrode is really, as experimentally determined, the potential,  $E_1$  of the cell



When a solution of unknown hydrogen-ion activity ( $x$ ) surrounds the hydrogen electrode the cell is



and the voltage arising is  $E_x$ . It is readily seen that, had the two cells been set up in opposed series, the cell reaction would have been equivalent to that of a cell in which hydrogen ion is transferred from a region of unit activity to a region of  $x$  activity.

$$\text{For this} \quad E = \frac{RT}{NF} \ln \frac{a_1}{a_2} = \frac{RT}{2.303NF} \log \frac{1}{a_x}$$

$$\text{But} \quad E = E_x - E_1$$

$$\log \frac{1}{a_x} = (E_x - E_1) \frac{2.303NF}{RT}$$

and at 25°C.  $RT/2.303NF$  for this case is 0.05915. Then

$$\log \frac{1}{a_x} = \frac{E_x - E_1}{0.05915}$$

If the activity could be taken equal to the concentration the above equation would offer a means of getting hydrogen-ion concentration. With this approximation

$$pH = 0.05915$$

Although at high values of  $pH$  it is probable that this is not greatly in error, commercial instruments are usually calibrated by comparison readings made on solutions of known  $pH$ .

For convenience most portable instruments for electrometric determination of  $pH$  contain no hydrogen electrode, but instead a glass, quinhydrone, or similar electrode. For each electrode the appropriate value for  $E_1$  must be used.



**Potentiometric Titrations.** In turbid or colored solutions where ordinary indicators would be useless, the hydrogen-ion end point may often be determined by electromotive-force measurements. This is possible because near the end point adding a small amount of standard solution will cause a large change in hydrogen-ion concentration and accordingly a large change in the voltage developed by a hydrogen electrode dipping into the solution. (See Figure 2.)

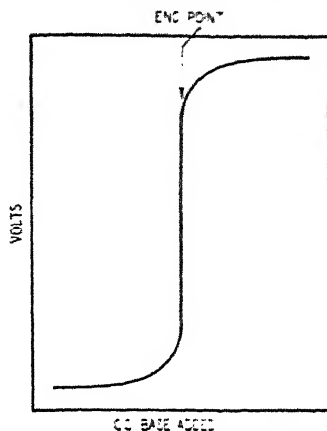


FIG. 2.

**Irreversible Processes.** In electrochemical changes of engineering importance various irreversible effects are encountered. These include overvoltage, polarization, and passivity, all of which were assumed absent in the reversible processes previously mentioned. A study of such details is part of the field of electrochemistry. As is so often true in thermodynamics, the results under reversible conditions will serve as a guide and limiting case for what may be expected in actual industrial processes.

## NOTATION FOR CHAPTER XIX

*Upper Case:*

<i>C</i>	Concentration
<i>E</i>	Reversible voltage of cell
<i>F</i>	One faraday = 96,494 coulombs
<i>F</i>	Free energy
<i>H</i>	Enthalpy
<i>K<sub>a</sub></i>	Equilibrium constant in terms of activity
<i>N</i>	Gram equivalents of material deposited
<i>R</i>	Gas constant
<i>T</i>	Absolute temperature
<i>T<sub>Cl</sub>, T<sub>H</sub></i>	Transference numbers for chloride and hydrogen ions
<i>W<sub>e</sub></i>	Electrical work

*Lower Case:*

<i>a</i>	Activity
<i>pH</i>	$\log_{10}[1/(\text{hydrogen-ion concentration})]$
<i>p</i>	Pressure

*Greek Letters:*

Activity coefficient

## PROBLEMS

1. If the reversible e.m.f. for the electrolysis of water is 1.23 volts at 1 atm. and 18°C., what do you estimate the reversible voltage to be for the same electrolysis carried out at 2000 lb./sq. in. pressure and 18°C.?
2. Repeat Problem 1, assuming the electrolysis to be carried out at 1 atm., but the temperature to be 90°C.
3. A potentiometric device for determining hydrogen-ion concentrations reads zero against a solution having a  $pH$  of 7 and 20 against a solution having a  $pH$  of 5. If the scale divisions are uniform and scale readings are proportional to voltage, approximately what will the instrument read in a solution having a  $pH$  of 4?
4. Explain why from a consideration of the thermodynamics involved it is economically possible to refine copper by electrolysis.

## CHAPTER XX

### THE THIRD LAW OF THERMODYNAMICS

Previous discussion has indicated the desirability of developing some method for determining free energy changes which would involve measurements of thermal properties only. As has been pointed out, integration of the expression

$$\left(\frac{\partial(\Delta F)}{\partial T}\right)_P = \frac{\Delta F - \Delta H}{T}$$

leads to an equation including a constant of integration, the value of which can be obtained only by making at least one equilibrium measurement. The principles to be presented in this chapter make possible evaluation of free energy effects from thermal data only.

**Analysis of the Problem.** The fundamental equation

$$\Delta F = \Delta H + T \left(\frac{\partial \Delta F}{\partial T}\right)_P$$

may be written in a somewhat different form by taking advantage of the fact that the pressure is constant. Since  $\left(\frac{\partial \Delta F}{\partial T}\right)_P = -\Delta S$ , and under constant pressure

$$\Delta S = \int_0^T \frac{\Delta C_p dT}{T} + C_0$$

simple substitution yields

$$\Delta F = \Delta H - T \left[ \int_0^T \frac{\Delta C_p dT}{T} + C_0 \right]$$

Certain important conclusions may be drawn from these equations: first, that at absolute zero either  $\Delta F$  must equal  $\Delta H$  or  $\left(\frac{\partial \Delta F}{\partial T}\right)_P$  must be infinite; secondly, that  $C_0$  is nothing more nor less than the entropy change at absolute zero for the process under discussion.

This constant,  $C_0$ , is not to be confused with the constant  $I$  previously mentioned in connection with the empirical expressions derived in Chapter XVII. The latter is of no theoretical significance, whereas the former, in the light of recent interpretations, appears to be a function of the fundamental properties of matter. By the third law principle, it is possible to arrive at definite conclusions regarding the value of  $\left(\frac{\partial(\Delta F)}{\partial T}\right)_-$  at  $T = 0$  and also in many cases to determine the value of  $C_0$ .

With this information, evaluation of free energy effects from thermal data is possible.

**Fundamental Assumptions.** Often in the history of thermodynamics empiricism had indicated results later justified by quantitative thinking. The third law is no exception to this, but unfortunately some of the earlier exact workers, in their enthusiasm, were led to unwarranted conclusions.

As early as 1881<sup>1</sup> Le Châtelier pointed out that the constant  $C_0$  was probably predictable from the physical properties of the substances entering into the reaction.

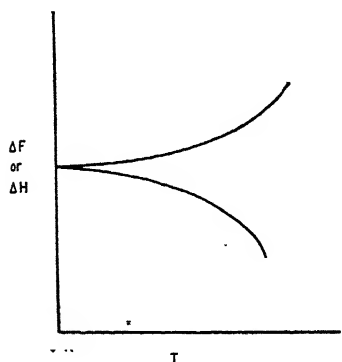


FIG. 1. Change in  $\Delta F$  or  $\Delta H$  with Temperature Near Absolute Zero.

In this country Lewis<sup>2</sup> and Richards<sup>3</sup> worked on the problem; in Europe, the work of Nernst<sup>4</sup> aroused an active interest.

From a study of the experimental data Nernst came to the conclusion that the values of  $\Delta F$  and  $\Delta H$  for any reaction involving only solids and liquids approach each other asymptotically as the temperature approaches absolute zero, the two curves fusing into one another at temperatures slightly above absolute zero. This is frequently expressed graphically by a plot similar to Figure 1.

The conclusions above stated are equivalent to saying that as absolute zero is approached both  $\Delta C_p$  and  $\Delta S$ , for reactions not involving gases, approach zero asymptotically.

<sup>1</sup> *Ann. Mines*, 13, 157 (1888). He also showed that the constant for a reaction equivalent to the sum of two or more reactions was the sum of the constants for the individual reactions.

<sup>2</sup> *Proc. Am. Acad.*, 35, 3 (1899).

<sup>3</sup> *Z. physik. Chem.*, 42, 129 (1902).

<sup>4</sup> *Nachr. kgl. Ges. Wiss., Göttingen, Math-physik. Klasse*, 1 (1906).

Lewis and Randall<sup>1</sup> point out that the statements of Nernst are open to objection and offer the empirical rule that for any solid or liquid at absolute zero

$$C_p = 0; \frac{C_p}{T} \text{ is zero or finite}$$

Low-temperature experimental work carried out during the last two decades seems to verify this conclusion.

**Conclusions.** From the results of the various investigations the following definite and seemingly exact statements may be formulated:

1. At absolute zero the entropy of any pure crystalline solid is zero.
2. Probably the difference in entropy between a pure substance in the crystalline and the amorphous states at absolute zero is small.
3. For supercooled liquids and solutions at absolute zero, the entropy is not zero, but may be small.

**Determination of Entropy.** The use of low-temperature calorimeters<sup>2</sup> capable of yielding precise results makes possible determination of heat capacities to within a few degrees of absolute zero. These data, in turn, enable one to construct a curve of the type given by Figure 2.

In constructing Figure 2 no monovariant changes were encountered, as the temperature dropped. These would have been represented by vertical "steps," and in evaluating entropy changes cognizance must be taken of these. Moreover, equilibrium conditions were assumed at all points. This is often a source of experimental difficulty, owing to the slow rates with which changes take place at low temperatures. For example, under such conditions sub-cooling is likely to be experienced and perhaps pass unnoticed, resulting in error.

To extend the curve to absolute zero, expressions for heat capacity based on quantum mechanics may be used. At low temperatures these simplify, without serious error, to

$$C_v = aT^3$$

where  $a$  is a characteristic constant for the substance under experiment.

<sup>1</sup> "Thermodynamics," p. 439.

<sup>2</sup> The use of magnetic fields to produce temperatures lower than are possible by transfer of heat to a cooling medium, such as a liquefied gas, is interesting from a pure science standpoint.

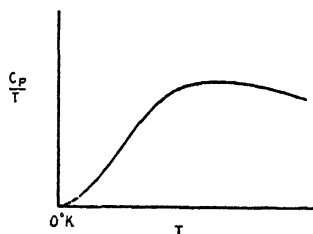


FIG. 2. Change in  $C_p/T$  with Temperature.

This is frequently referred to as the Debye rule, although Einstein has developed formulas which lead to the same conclusion.

Since

$$\Delta S_P = \int_0^x \frac{C_p}{T} dT$$

by integration Figure 2 yields the value of  $\Delta S$  between  $0^\circ\text{K.}$  and any desired temperature. If in addition the value of  $S$  is known at absolute zero, this added to  $\Delta S$  as above calculated gives the value for the absolute entropy. In this way it is possible to formulate a table of absolute entropies.

Of late years, especially for the more simple gaseous molecules, methods of calculating entropies from spectroscopic data have been developed and utilized. These give means for extending and in many cases checking the results from low-temperature calorimetric work.

Based on theoretical considerations several general equations for the absolute entropies of specific substances at any temperature have been developed. These are interesting, but since they are limited to a few of the more simple molecules, they are not of general importance to the engineer.<sup>1</sup>

**Significance of Absolute Entropy.** It is reasonable to consider the entropy of a substance as a positive finite quantity. Just as any body, in a chosen condition, has a finite definite volume and contains a fixed amount of energy, it also has a fixed absolute positive entropy. For any material this may be decreased by decreasing temperature or by increasing pressure.

### SUMMARY

1. At absolute zero the entropy of a pure crystalline solid is zero. The entropy of matter in other forms may become zero at absolute zero, but in general nothing definite can be said concerning this, except that entropies cannot become negative.

2. The absolute entropies of the various substances entering into a reaction being known, from thermal (calorimetric) data alone, the free energy change at any condition may be calculated.

### NOTATION FOR CHAPTER XX

#### *Upper Case:*

- C* Heat capacity; also a constant as  $C_0$
- F* Free energy
- H* Enthalpy
- S* Entropy
- T* Absolute temperature

<sup>1</sup> See Taylor's "Treatise on Physical Chemistry," 2nd Ed., pp. 1426-1450, New York, Van Nostrand, 1930, and Lewis and Randall's "Thermodynamics," pp. 455-458.

*Lower Case:*

$a$  A constant

*Subscripts:*

$P, p$  Constant pressure

$v$  Constant volume

*Greek Letters:*

$\Delta$  Final value — Initial value; also Resultants — Reactant





## APPENDIX

TABLE I  
EQUIVALENTS FOR CONVERTING UNITS

Mass:      1 pound = 453.59 grams

Pressure: 1 atmosphere = 760 millimeters mercury  
                               = 29.921 inches mercury  
                               = 33.934 feet water (60°F.)  
                               = 14.696 pounds per square inch

Energy:    1 joule =  $10^7$  dyne-centimeters =  $10^7$  ergs  
                               = 1 watt-second

1 calorie = 4.1861 joules

1 British thermal unit (B.t.u.) = 251.996 calories  
   = 778.26 foot-pounds

1 Centigrade heat unit (C.h.u.) = 1.8 British thermal units

1 horsepower-hour = 2544.1 British thermal units

1 kilowatt-hour = 3412.75 British thermal units

Power:     1 watt = 1 joule per second  
                               = 4.1861 calories per second

1 horsepower = 550 foot-pounds per second  
                               = 33,000 foot-pounds per minute  
                               = 178.08 calories per second

1 kilowatt     = 1000 watts  
                               = 1.3415 horsepower

Heat Capacity and Entropy

$$1 \frac{\text{B.t.u.}}{(\text{lb.})(^\circ\text{F.})} = 1 \frac{\text{gm. cal.}}{(\text{gm.})(^\circ\text{C.})} = 1 \frac{\text{C.h.u.}}{(\text{lb.})(^\circ\text{C.})}$$

TABLE II

EQUATIONS FOR MOLAL HEAT CAPACITIES OF GASES AT CONSTANT PRESSURE\*

Gas	Equation, $T = ^\circ\text{K.}$	Error, %	Temperature Range, $^\circ\text{K.}$
A, He, Ne, Xe	4.97	Nil	All
CH <sub>4</sub> .....	$5.34 + 11.5 \times 10^{-3}T$	2	273–1200°
Cl <sub>2</sub> .....	$8.28 + 0.56 \times 10^{-3}T$	1.5	273–2000°
CO.....	$6.60 + 1.20 \times 10^{-3}T$	2	273–2500°
CO <sub>2</sub> .....	$10.34 + 2.74 \times 10^{-3}T - 1.995 \times 10^{-5}T^{-2}$	1.5	273–1200°
F <sub>2</sub> .....	$6.50 + 1.00 \times 10^{-3}T$	5	300–3000°
H <sub>2</sub> .....	$6.62 + 0.81 \times 10^{-3}T$	2	273–2500°
HBr.....	$6.80 + 0.84 \times 10^{-3}T$	2	273–2000°
HCl.....	$6.70 + 0.84 \times 10^{-3}T$	1.5	273–2000°
HI.....	$6.93 + 0.83 \times 10^{-3}T$	2	273–2000°
H <sub>2</sub> S.....	$7.20 + 3.60 \times 10^{-3}T$	5–10	300–600°
N <sub>2</sub> .....	$6.50 + 1.00 \times 10^{-3}T$	3	300–3000°
NH <sub>3</sub> .....	$6.70 + 6.30 \times 10^{-3}T$	1.5	300–800°
NO.....	$8.05 + 0.233 \times 10^{-3}T - 1.563 \times 10^{-5}T^{-2}$	2	300–5000°
O <sub>2</sub> .....	$8.27 + 0.258 \times 10^{-3}T - 1.877 \times 10^{-5}T^{-2}$	1.5	300–5000°
SO <sub>2</sub> .....	$7.70 + 5.30 \times 10^{-3}T - 0.83 \times 10^{-6}T^2$	2.5	300–2500°

\* Kelley, U. S. Bureau of Mines, Bulletin 371, 1934.

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